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by

D. W. Fuerstenau and T. W. Healy
Principal Investigators

FINAL REPORT

to

Federal Water Pollution Control Administration
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ABSTRACT

With the use of biodegradable detergents and subsequent lowering of the detergent level in waste waters, less attention has been focused on the interaction of detergents with colloidal solids. Still several factors pointed out the desirability for basic studies on detergent adsorption at polar solid-water interfaces. Detergent ions must be retained at enzyme surfaces during the biodegradation operation in sludge treatment. Since these wastes must pass naturally through soils on their way to water courses of various kinds, adsorption phenomena on the polar solids constituting soils are of considerable importance. The removal of micro-organisms from water systems by flotation techniques is becoming increasingly important and the eventual fate of the flotation collector must be defined. Further, the mechanism of adsorption of amphipathic molecules in water treatment and rennovation processes is poorly understood. The research results presented in this report were thus obtained to further the basic understanding of such adsorption phenomena related to the interaction of detergent in aqueous systems with polar colloidal solids. This research has been carried out using alumina as a model polar oxide solid together with well-characterized sulfonates as the detergent.

The effects of hydrocarbon chain length on sulfonate adsorption have been studied and two distinct adsorption mechanisms delineated. Good quantitative agreement has been obtained between the observed effects and theoretical considerations based on the Stern-Grahame model of the electrical double layer at the solid-water interface. The thermodynamics of adsorption have been investigated by measurement of the heat of immersion of alumina into aqueous surfactant solutions and a model for sulfonate adsorption onto a hydrated alumina surface has been presented. The aggregation of colloidal alumina in the presence of adsorbed surfactants was studied as a function of temperature and pH. Coagulation was shown to result from reduction of the diffuse layer potential due to adsorption. Studies of the adsorption of alkylaryl sulfonates have indicated that the benzene ring exhibits an effect similar to the presence of three additional CH_2 groups and also reduces the pH sensitivity of the adsorption process considerably. The very important role of pH in controlling surface potential and surface charge and thereby the adsorption of alkyl detergents was investigated. Finally, our studies delineated conditions under which inorganic electrolytes compete with the adsorption of detergents at oxide-water interfaces.

INTRODUCTION

Even with the change to the more linear sulfonates as detergents, waste water-treatment effluents still contain appreciable concentrations of ionic detergents. Water supplies containing such detergents must pass naturally through soils on their way to water courses of various kinds, and adsorption phenomena on polar solids constituting the soils are then of great importance. Furthermore, a number of processes for detergent removal have been suggested involving adsorption steps in their operation. With this great need for understanding adsorption in these systems, a surprisingly limited amount of basic research has been carried out on the adsorption of organic electrolytes at solid-water interfaces. In order to obtain basic information that can be of value in effective programs for water treatment, the aims of our research program were to study (1) the nature of the adsorbate-adsorbent bond between alkyl and alkylaryl sulfonates and polar solids, (2) the configuration of the molecule at the interface, (3) the effect of structure of the hydrocarbon chain on adsorption reactions, (4) the effect of properties of the solid adsorbent itself on the adsorption process, (5) the mechanism by which inorganic ions affect the adsorption of the organic electrolytes, (6) the thermodynamics of these systems.

The adsorption of alkylbenzene sulfonates (ABS) on nonpolar materials such as activated carbon and organic materials such as cotton and nylon has received considerable attention. Reviews of progress in this area have been published[1-3]; and specific details of mechanisms, thermodynamics, and kinetics of adsorption of alkylaryl sulfonates on carbon and organics have been presented in the published literature[4-8].

In addition to the use of activated carbon in an adsorption process, a number of processes involving polar solids have been suggested for removal of detergents from polluted waters, including adsorption on activated alumina[4], adsorption on inorganic ion exchangers[9], the purposeful addition of inorganic particles for detergent adsorption followed by flotation[10].

Further, detergent molecules must be retained at enzyme surfaces during the biodegradation operation in sludge treatment. Also, the removal of micro-organisms from water systems by flotation would necessitate defining the eventual fate of the flotation collector. Thus, it was apparent that to understand the mechanism of adsorption of amphipathic molecules in water treatment in general requires fundamental knowledge of adsorption systems involving detergent interaction with polar colloidal materials.

Search of the literature indicated a great lack of fundamental work on the adsorption of detergents on polar solids. Some work by colloid chemists on their traditional colloid material, namely silver iodide, has been reported[11]. However, silver iodide appears to be partially hydrophobic[12] and its behavior cannot be correlated with that of polar oxides. Of the limited investigations with polar oxides, there appears to be some confusion as to how the detergent may be adsorbing at the water-solid interface[13]. The preliminary studies of Wayman[14, 15, 16, 17] on the adsorption of ABS on soils and clay minerals was the first significant attempt to ascertain details of detergent adsorption by soil minerals. Bendixen and others[18] also reported on studies using soils for detergent removal. Since every natural water system has dissolved metal ions, it is of importance that how these ions affect surfactant adsorption be known. Flotation studies show that metal ions do have marked control of the adsorption of sulfonates on such polar solids as quartz and silicates, and only recently has a meaningful explanation of this particular process been put forth[19].

Ultimate solution of the problems associated with the removal of detergents from polluted waters will come with our understanding of the basic principles that control adsorption of surfactants at solid-water interfaces. The results of this research should add to the background of necessary fundamental information on detergent adsorption from water. In this program, alumina has been used as a model polar solid together with well characterized alkyl and alkylaryl sulfonates as adsorbates.

The report is presented as six separate sections, and each section describes the results of one separate research investigation in detail. The sections are the following:

Section 1. "The Effect of Hydrocarbon Chain Length on the Adsorption of Sulfonates at the Solid-Water Interface"

This was presented at the Symposium on Adsorption from Aqueous Solution, American Chemical Society, Division of Water, Air, and Waste Chemistry and Division of Colloid and Surface Chemistry, Chicago, September 1967, and is to be published in an Advances to Chemistry Series.

Section 2. "The Aggregation of Colloidal Alumina Dispersions by Adsorbed Surfactant Ions"

This has been published in the Journal of Colloid and Interface Science, Vol. 22, pp. 599-605 (1966).

Section 3. "The Heat of Immersion of Alumina into Aqueous Sodium Dodecyl Sulfonate Systems"

This has been accepted for publication in the Journal of Colloid and Interface Science.

Section 4. "The Adsorption of Alkylbenzene Sulfonates at the Alumina-Water Interface"

This will eventually be submitted to Environmental Science and Technology.

Section 5. "The Effect of Surface Charge on the Adsorption of Sodium Dodecyl Sulfonate by an Oxide Adsorbent"

After more detailed analysis, this will be prepared as a manuscript for the Journal of Colloid and Interface Science.

Section 6. "The Effect of Inorganic Electrolytes on Detergent Adsorption at Water-Solid Interfaces"

This may eventually be prepared as a short technical note.

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SECTION 1

THE EFFECT OF HYDROCARBON CHAIN LENGTH ON THE ADSORPTION OF SULFONATES AT THE SOLID-WATER INTERFACE

by

T. Wakamatsu* and D. W. Fuerstenau**

ABSTRACT

Isotherms for the adsorption at the alumina-water interface of sodium alkyl sulfonates containing 8, 10, 12, 14, and 16 carbon atoms were determined at constant pH, temperature, and ionic strength. Electrophoretic mobilities were measured for the same conditions. It is clearly shown that the adsorption isotherm for such detergents consists of three distinct regions. In Region 1 where adsorption occurs by ion exchange with chloride ions used to control ionic strength, the isotherms are approximately characterized by the same line. The onset of the increased adsorption due to association of adsorbed detergent ions denoting Region 2 depends on the hydrocarbon chain length. In Region 3, the electrokinetic potential is reversed and the isotherms exhibit a decreased dependence on concentration because of electrostatic repulsion at the surface. By means of the Stern-Grahame model, the free energy of interaction of hydrocarbon chains at the interface is calculated to be -0.95 RT per mole of CH_2 groups.

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The adsorption of ionic surfactants at solid-water interfaces is of great technological importance in such diverse fields as water renovation, detergency, mineral flotation, and corrosion inhibition. The complex nature of the adsorption of surfactants at the solid-water interface is controlled by the nature of the adsorbing species itself, the properties of the solid adsorbent, and the composition of the aqueous solution. Dependent on these factors, surfactant-solid systems can be classified into two broad types, namely 1) those in which the surfactant is adsorbed as a counter ion in the double layer through coulombic interaction with the surface charge and 2) those in which the surfactant adsorbs by covalent bond formation with atoms in the solid surface. In such adsorption processes, and also in other interfacial phenomena, the length of the hydrocarbon chain of the surfactant plays a dominant role in the behavior of the system. This present investigation is concerned with the adsorption of alkyl sulfonates at the alumina-water interface, a system in which the surfactant adsorbs as counter ions in the electrical double layer. In particular, the role of the hydrocarbon chain in the adsorption process has been studied by maintaining adsorption conditions constant, namely pH, ionic strength, and temperature, for a series of alkyl sulfonates with varying chain lengths.

The dominant role of the hydrocarbon chain in the adsorption of alkylammonium salts has been demonstrated by electrokinetic experiments[1], flotation behavior[2], and by adsorption measurements[3]. Recently[4], it was demonstrated that the isotherm for the adsorption of sodium dodecyl sulfonate at the alumina-water interface is characterized by three distinct regions: 1) Region 1 in which the detergent ions adsorb individually through coulombic attraction for the surface, 2) Region 2 in which the adsorption is enhanced through association of the hydrocarbon chains of the adsorbed surfactant ions, and 3) Region 3 in which the charge in the Stern plane exceeds the surface charge with the resulting electrostatic repulsion acting to retard adsorption. In particular,

our purpose has been to determine how each of these adsorption regions depends on the hydrocarbon chain of the surfactant.

EXPERIMENTAL MATERIALS AND METHODS

For the solid adsorbent, alpha-alumina (Linde "A") of 99.95 percent purity was used. Its specific surface area, as measured by krypton gas adsorption and by stearic acid adsorption from benzene, was found to be 15 m^2/gram. Its zero point of charge occurs at pH 9.1. The alkyl sulfonates were prepared by neutralizing high purity sulfonic acids (C8, C10, C12, C14, and C16) with sodium hydroxide and by recrystallizing the sodium salt from hot absolute ethyl alcohol. All inorganic chemicals were reagent grade. Conductivity water prepared in a quartz still was used for all solutions.

The adsorption experiments were carried out in a 600 ml beaker that was stoppered with a Teflon disc containing holes for a thermometer, gas inlet and outlet, and pH electrodes. The cell containing the alumina and the surfactant solution was maintained at a constant temperature by immersing the cell in a thermostatically controlled water bath. An atmosphere of purified nitrogen was maintained over the cell. The experimental conditions were held constant at pH 7.2, 25°C, and 2×10^{-3}M ionic strength (adjusted with sodium chloride). The system was stirred by means of a magnetic, Teflon-covered stirring bar for four hours. About 2 hours was required for adjusting pH, and the remaining time was used for attaining equilibrium and for sampling. The method used for the determination of sulfonate concentration is the well-known methylene blue complex method[5].

Electrophoretic mobilities of the alumina particles were determined for the same conditions as were used to obtain the adsorption isotherms. For this purpose, a sample of the alumina suspension was

transferred to the electrophoresis cell for measurement of the electrophoretic mobilities. A Zeta-Meter was used for this part of the program.

EXPERIMENTAL RESULTS

The isotherm for the adsorption of sodium dodecyl sulfonate by alumina at constant pH (pH 7.2) and ionic strength (2×10^{-3} M) is given in Figure 1 to illustrate specifically the nature of the isotherm obtained for the adsorption of a detergent from aqueous solution. In this figure, the amount of sulfonate adsorbed per unit area of alumina is plotted logarithmically as a function of the equilibrium concentration of alkyl sulfonate in solution. The adsorption isotherm consists of three distinct regions: Region 1, which is characterized by a low increase in adsorption with increasing surfactant concentration; Region 2, by an abrupt increase in the slope of the isotherm; and Region 3, again by a decreased dependence of adsorption on sulfonate concentration. To correlate changes in the adsorption process with the isotherm, the electrophoretic behavior of alumina in the presence of sodium dodecyl sulfonate is also included in Figure 1. In Figure 2, isotherms for the adsorption of C8 to C16 sulfonates are presented to show how the chain length of the detergent affects the adsorption process.

The electrophoretic mobilities of alumina for the same conditions as used for determination of the isotherms is presented in Figure 3. This figure, together with Figures 1 and 2, shows that the mobility is positive in sign in Regions 1 and 2 but is negative in Region 3. Region 1 is characterized by the electrophoretic mobility being nearly independent of the sulfonate concentration. The transition between Region 1 and Region 2 is marked by a sharp change in the electrophoretic mobility-vs-concentration curve whereas the transition between Regions 2 and 3 occurs at concentrations where the mobility is zero. Clearly, the electrophoretic behavior of the alumina depends markedly on the number of carbon atoms in the hydrocarbon chain of the detergent.

DISCUSSION OF RESULTS

The Adsorption Isotherm

In a previous paper[4], it was shown that the isotherm for the adsorption of a detergent at the solid-water interface can be characterized by three distinct regions but at that time the data were not analyzed statistically. Statistical analysis of the data presented in Figure 1 shows that the isotherm corresponding to each of the three regions is characterized by the following straight lines:

$$\text{Region 1:} \quad \log \Gamma = -8.76 + 0.66 \log C$$
$$\text{Region 2:} \quad \log \Gamma = -3.30 + 1.92 \log C$$
$$\text{Region 3:} \quad \log \Gamma = -8.03 + 0.60 \log C$$

Statistical analysis of these data shows that the slope of these three straight lines at the 95 percent confidence level[6] is 0.66 ± 0.19, 1.92 ± 0.25, and 0.60 ± 0.22 for Regions 1, 2, and 3, respectively. Region 1 for sodium dodecyl sulfonate under these experimental conditions applies up to a detergent concentration of 6×10^{-5} M. The adsorption is characterized by Region 2 between 6×10^{-5} M and 3×10^{-4} M under these conditions, and by Region 3 above 3×10^{-4} M sulfonate.

Further evidence for three distinct modes of adsorption can be seen in the electrophoretic behavior of alumina in the presence of sodium dodecyl sulfonate. Below 6×10^{-5} M, the electrophoretic mobility is nearly independent of concentration, but at this concentration the slope of the mobility-vs-concentration curve abruptly changes. At 3×10^{-4} M dodecyl sulfonate concentration, the electrophoretic mobility reverses its sign, indicating that the charge in the Stern layer now exceeds the surface charge in absolute magnitude.

This experimental evidence clearly shows the complicated nature of the adsorption isotherm for a detergent at the polar solid-aqueous solution interface.

The Effect of Alkyl Chain Length on Adsorption

Figure 2 shows that the adsorption isotherms all have somewhat the same general characteristics only the concentrations at which the effects

occur appear to depend on the alkyl chain length. Consequently, the adsorption behavior in each of the three regions of the isotherms will be discussed separately and will be interpreted in terms of the role that the hydrocarbon chain plays in the adsorption process.

It has already been established[4] that alkyl sulfonate ions adsorb at the positively charged alumina-water interface as counter ions in the electrical double layer. Chemisorption is absent. The electrical double layer model will then be used to interpret the adsorption behavior observed in these experiments.

In Region 1, alkyl sulfonate ions are considered to adsorb as individual counter ions in competition with the chloride ions used to control the ionic strength. On the other hand, Figures 2 and 3 show that the adsorption of C8 sulfonate is restricted entirely to Region 1.

If the adsorption is of non-associated sulfonate ions by ideal exchange in the diffuse layer, a single line independent of chain length should characterize the adsorption in Region 1. For the C16 sulfonate, at the lowest concentration which could be studied, the adsorption already has exceeded that of Region 1. For C8, C10, C12, and C14 this adsorption is characterized approximately by a single line, whose slope is 0.6 instead of the expected slope of 1.0. Except for the C8 detergent, the slope of each individual isotherm is about 0.7. Such deviations from ideal exchange are not yet clearly understood but are considered to reflect differences in the ability of surfactant ions compared to chloride ions to penetrate the diffuse layer region. This is a subject of continued research.

Region 2 is characterized by a marked change in the slope of the adsorption isotherms. This results from the onset of association of the hydrocarbon chains of the surfactant ions adsorbed in the Stern plane. The mean separation distance of adsorbed ions under these conditions is about 70 A, which approximates the mean separation distance in bulk at the cmc. This association, which has been called hemimicelle formation[7], gives rise to a specific adsorption potential which causes the adsorption to increase

markedly and brings about a reversal in the sign of the potential at the Stern plane. The hemimicelle concentration, that is the bulk concentration necessary to induce association in the interface, increases with decreasing chain length. At pH 7.2 on alumina this concentration is 4×10^{-6} M for C16, 1.4×10^{-5} M for C14, 6×10^{-5} M for C12, 7×10^{-4} M for C10, and is above 2×10^{-3} M for C8 sulfonate. The slopes of the isotherms are 0.56 for C8, 1.33 for C10, 1.92 for C12, 2.50 for C14, and 5.80 for C16 sulfonate. Thus, with increasing chain length, the competition between RSO_3^- and Cl^- for sites at the surface strongly favors the adsorption of the detergent.

In a previous publication[4] it was shown that adsorption in Region 2 where association of the hydrocarbon chains is leading to extensive adsorption and eventual reversal of the sign of the mobility (i.e. ψ_δ), is given by

$$\Gamma_\delta = 2rC \exp\left[\frac{-zF\psi_\delta - n\phi}{RT}\right] \qquad (1)$$

where Γ_δ is the adsorption density in the Stern plane in moles/cm^2, r is the effective radius of the adsorbed ion, C is the bulk concentration in moles/cm^3, z is the valence of the adsorbed ion, F is Faraday's constant, ψ_δ is the potential in the Stern plane, ϕ is the cohesive energy per mole of CH_2 groups, n is the effective number of associating CH_2 groups per hydrocarbon chain, R is the gas constant, and T the absolute temperature. Thus, expressing adsorption on a logarithmic basis, we have

$$\frac{d \ln \Gamma}{d \ln C} = 1 - \frac{zF}{RT} \frac{d\psi_\delta}{d \ln C} - \frac{\phi}{RT} \frac{dn}{d \ln C} \qquad (2)$$

The variation of n with concentration expresses the fact that in Region 2 complete removal of each CH_2 group of the surfactant from water is only possible at a monolayer. In bulk systems the analogous processes are the pre-association into dimers, trimers, etc. just below the critical micelle concentration.

From the slopes of the adsorption isotherms and the mobility-concentration curves, it is possible to evaluate with Equation 2, $dn/d\ln C$, i.e. the term which expresses the effective number of CH_2 groups removed from the aqueous environment. By this means, the values of $dn/d\ln C$ are found to be 9 for C16, 4 for C14, 2 for C12, 2 for C10, and 0 for C8. A comparison can be made for the C16 sulfonate by considering the mobility curves and adsorption isotherms. Observation of the electrophoretic mobility curve for the C16 surfactant shows that hemimicelle formation begins at 6×10^{-6}M and that the mobility curve again becomes independent of concentration at 1.5×10^{-5}M, this latter concentration coinciding with monolayer coverage in the expected manner. Thus, n has an effective value of zero at about 6×10^{-6}M and a value of 15 at monolayer coverage (assuming that the terminal CH_3 groups are exposed to the solution). This leads to an estimated value of $dn/d\ln C$ of approximately 16. As pointed out previously[4], a limitation of this treatment is that throughout Region 2, the fraction of the sulfonate ions that adsorb in the Stern layer increases, reaching unity at the end of Region 2. Since Equation 2 depends on the assumption that the adsorption in the Stern layer is proportional to the total adsorption, the value of $dn/d\ln C$ calculated from the adsorption will be too low.

The end of Region 2 is characterized by the fact that the mobility passes through zero. When the mobility is zero, the Stern-Grahame expression for the adsorption of a specifically adsorbing surfactant ion can be expressed as

$$\left(\Gamma_\delta\right)_o = 2r\, C_o \exp\left(-\frac{N\phi}{RT}\right) \qquad (3)$$

where N is the number of carbon atoms in the hydrocarbon chain. Here we must assume that the effective fraction of the CH_2 groups

removed from aqueous environment when ψ_δ is zero must be independent of chain length. Putting Equation 3 in logarithmic form and rearranging terms yields:

$$\ln C_o - \ln \frac{(\Gamma_\delta)_o}{2r} = -N \frac{\phi}{RT} \qquad (4)$$

The numerical values of $(\Gamma_\delta)_o$ and C_o are tabulated in the following table:

	$(\Gamma_\delta)_o$	C_o
C16	1.6×10^{-10} mole/cm^2	1.0×10^{-5} mole/l
C14	1.1×10^{-10}	9.0×10^{-5}
C12	7.9×10^{-11}	2.8×10^{-4}
C10	6.0×10^{-11}	1.7×10^{-3}

From these numbers, it can be seen that the change of $(\Gamma_\delta)_o$ when increasing the number of CH_2 groups in the alkyl chain length from C10 to C16, is 6.0×10^{-11} to 1.6×10^{-10}, while the variations in the values of $(C_\delta)_o$ is 10^{-5} to 1.7×10^{-3}. We do not know the effective radius of each sulfonate ion at zero mobility, but it certainly must correspond approximately to the thickness of the adsorbed layer. Perhaps it may even increase with the number of carbon atoms in the hydrocarbon chain. However, as the variation in the value of $(C_\delta)_o$ is very large compared to that of $(\Gamma_\delta)_o$, it will be assumed that $\ln (\Gamma_\delta)_o/2r$ is a constant independent of the chain length. Thus, if we plot the logarithm of $(C_\delta)_o$ against N, a straight line should be obtained. Accordingly, in Figure 4, the concentration of sodium alkyl sulfonate in solution corresponding to zero mobility is plotted as a function of the number of carbon atoms in the alkyl chain. From the slope of this line, the value of ϕ is calculated to be $-0.95RT$, a value in good agreement with previous studies of amine salts on quartz[1,2].

In Region 3 the slope of the isotherm is lower than in Region 2. Here the surfactant ions probably adsorb by a somewhat different mechanism. As shown in Figure 2, the values of ψ_δ must be negative in this region, and consequently the adsorbed sulfonate ions should be subjected to electrostatic repulsion in the adsorption process. Thus reducing the slope of the isotherms in this region. In Region 3 the slope of the C16 isotherm is 2.16, that of the C14 is 1.50 and that of the C12 isotherm is 0.60. Although only three values for this slope could be obtained from our studies, it is apparent that the value becomes greater with increasing hydrocarbon chain length. This tendency again can be attributed to the increased attraction between hydrocarbon chains with increase in chain length. Further, the adsorbed detergent may tend to orient differently at the surface because of the electrostatic repulsion upon reversal of ψ_δ .

SUMMARY

As a part of a study on the mechanism of adsorption of alkyl sulfonates at the alumina-water interface, the role of hydrocarbon chain length in the adsorption process has been investigated by adsorption and electrophoresis measurements with sodium alkyl sulfonates containing 8, 10, 12, 14, and 16 carbon atoms at constant pH, temperature, and ionic strength. The adsorption isotherms have clearly been shown to consist of three distinct regions, depending upon the intermolecular behavior of the hydrocarbon chain. In Region 1 where the detergent ions adsorb in the double layer in competition with the chloride ions used to control ionic strength, the isotherms are characterized by approximately the same straight line. In Region 2 the adsorbed detergent ions associate, resulting in a sharp increase in the adsorption density. The onset of this association occurs at lower bulk concentrations as the

hydrocarbon chain length is increased. In Region 3 the adsorption isotherms again have a decreased slope; in this region the electrokinetic potential is reversed, resulting in electrostatic repulsion between the adsorbed ions. By means of the Stern-Grahame model of the double layer under conditions where the electrophoretic mobility of the alumina is zero, the cohesive free energy per mole of CH_2 groups has been calculated to be $-0.95\ RT$.

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LIST OF FIGURE CAPTIONS

Figure 1. The electrophoretic behavior and isotherm for the adsorption of sodium dodecyl sulfonate from aqueous solution at pH 7.2, 25°C, and 2×10^{-3} M ionic strength (NaCl). The 95% confidence limits for the three straight-line regions of the adsorption isotherm are shown.

Figure 2. Adsorption isotherms for sodium alkyl sulfonates of different hydrocarbon chain lengths on alumina at pH 7.2, 25°C, and 2×10^{-3} M ionic strength.

Figure 3. The electrophoretic mobility of alumina at pH 7.2 and 2×10^{-3} M ionic strength as a function of the concentration of sulfonates with various hydrocarbon chain lengths.

Figure 4. Variation of the concentration of sulfonate necessary for zero electrophoretic mobility of alumina as a function of the number of carbon atoms in the alkyl chain.

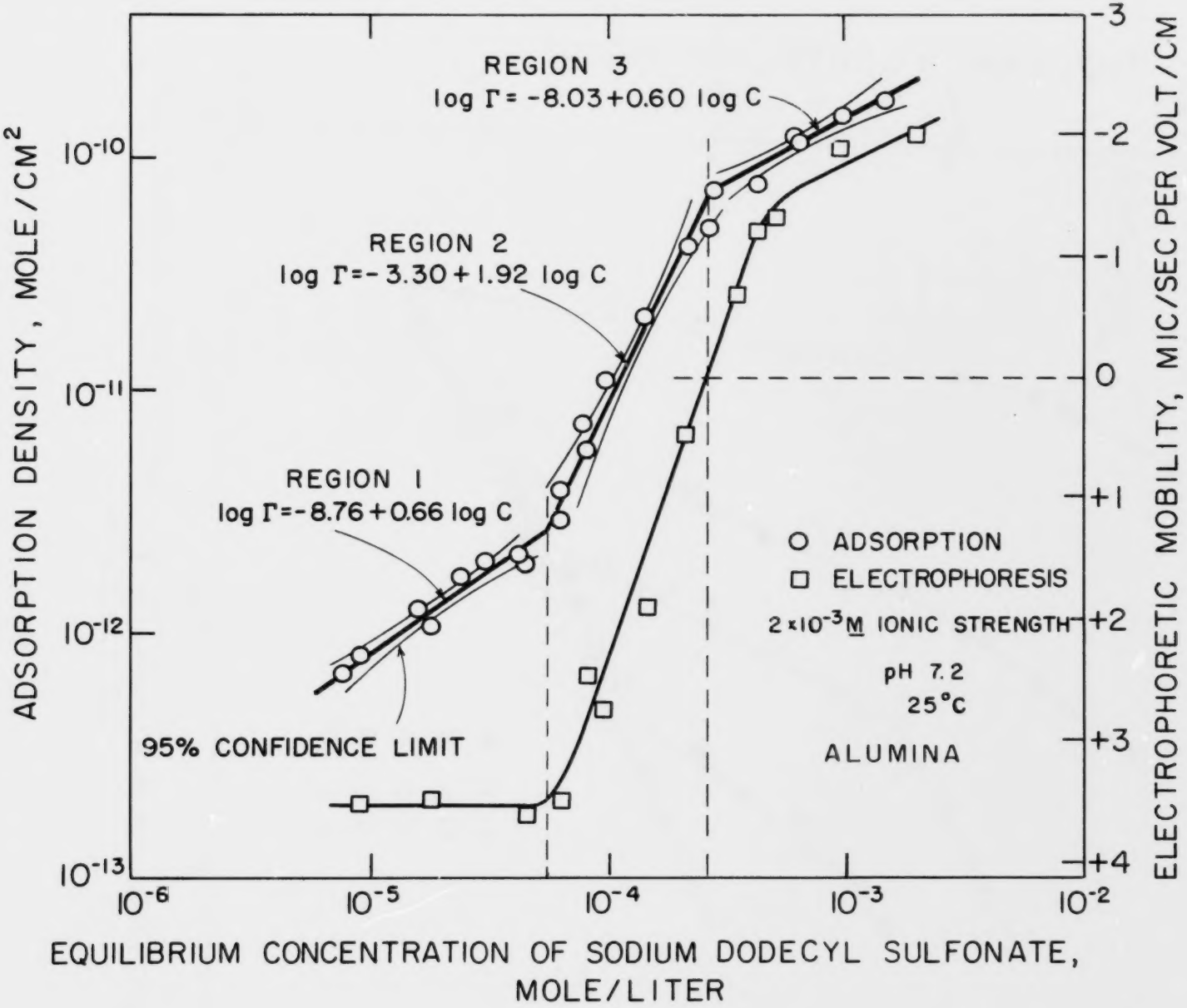

REGION 3
log Γ = -8.03+0.60 log C
REGION 2
log Γ=- 3.30 + 1.92 log C
REGION 1
log Γ=- 8.76 + 0.66 log C
95% CONFIDENCE LIMIT
O ADSORPTION
□ ELECTROPHORESIS
2×10⁻³M IONIC STRENGTH
pH 7.2
25°C
ALUMINA
ADSORPTION DENSITY, MOLE/CM²
ELECTROPHORETIC MOBILITY, MIC/SEC PER VOLT/CM
EQUILIBRIUM CONCENTRATION OF SODIUM DODECYL SULFONATE, MOLE/LITER
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
10⁻²
-3
-2
-1
0
+1
+2
+3
+4

FIGURE 1

FIGURE 2

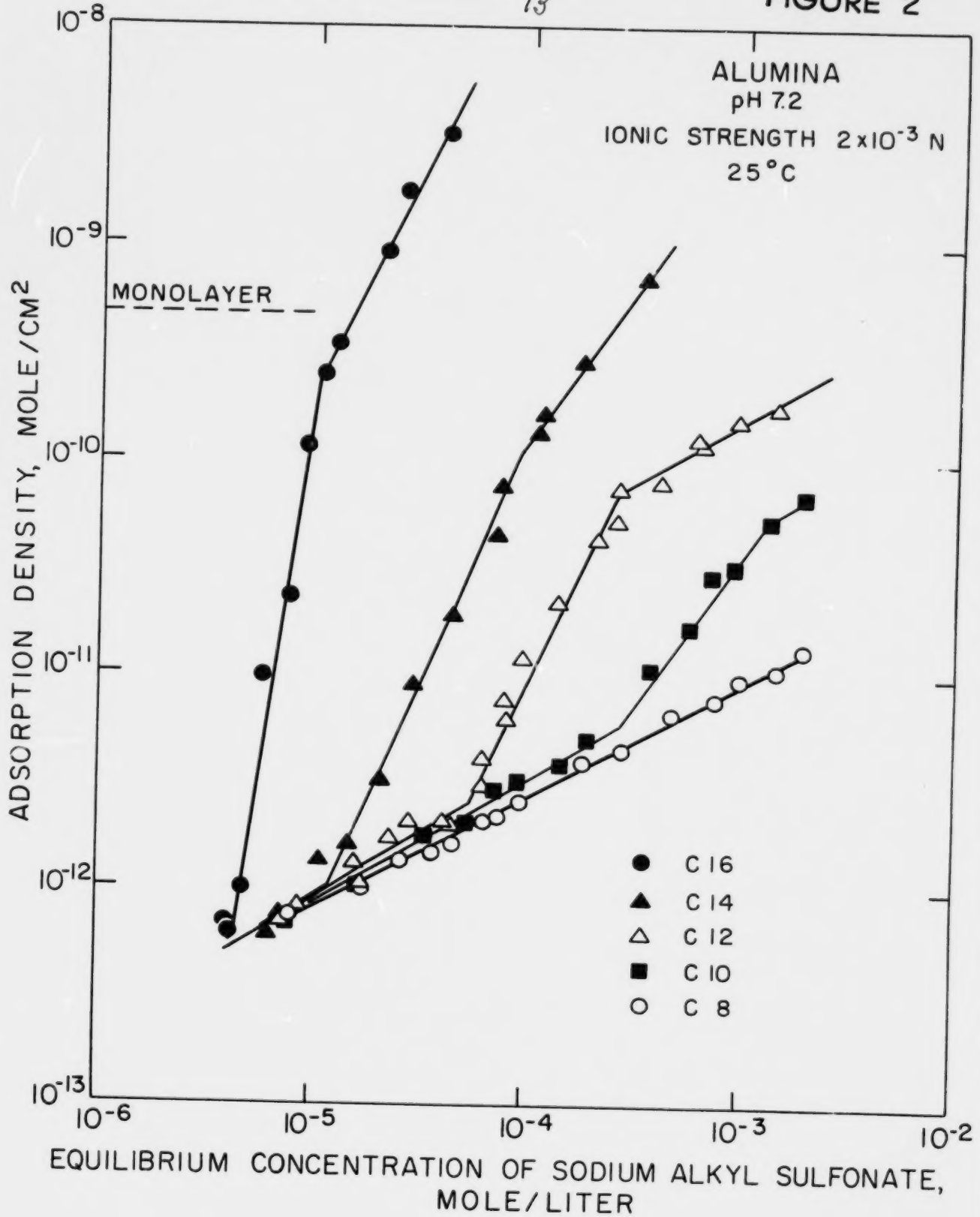

ALUMINA
pH 7.2
IONIC STRENGTH 2x10⁻³ N
25°C
MONOLAYER
ADSORPTION DENSITY, MOLE/CM²
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
C 16
C 14
C 12
C 10
C 8
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
10⁻²
EQUILIBRIUM CONCENTRATION OF SODIUM ALKYL SULFONATE, MOLE/LITER

FIGURE 3

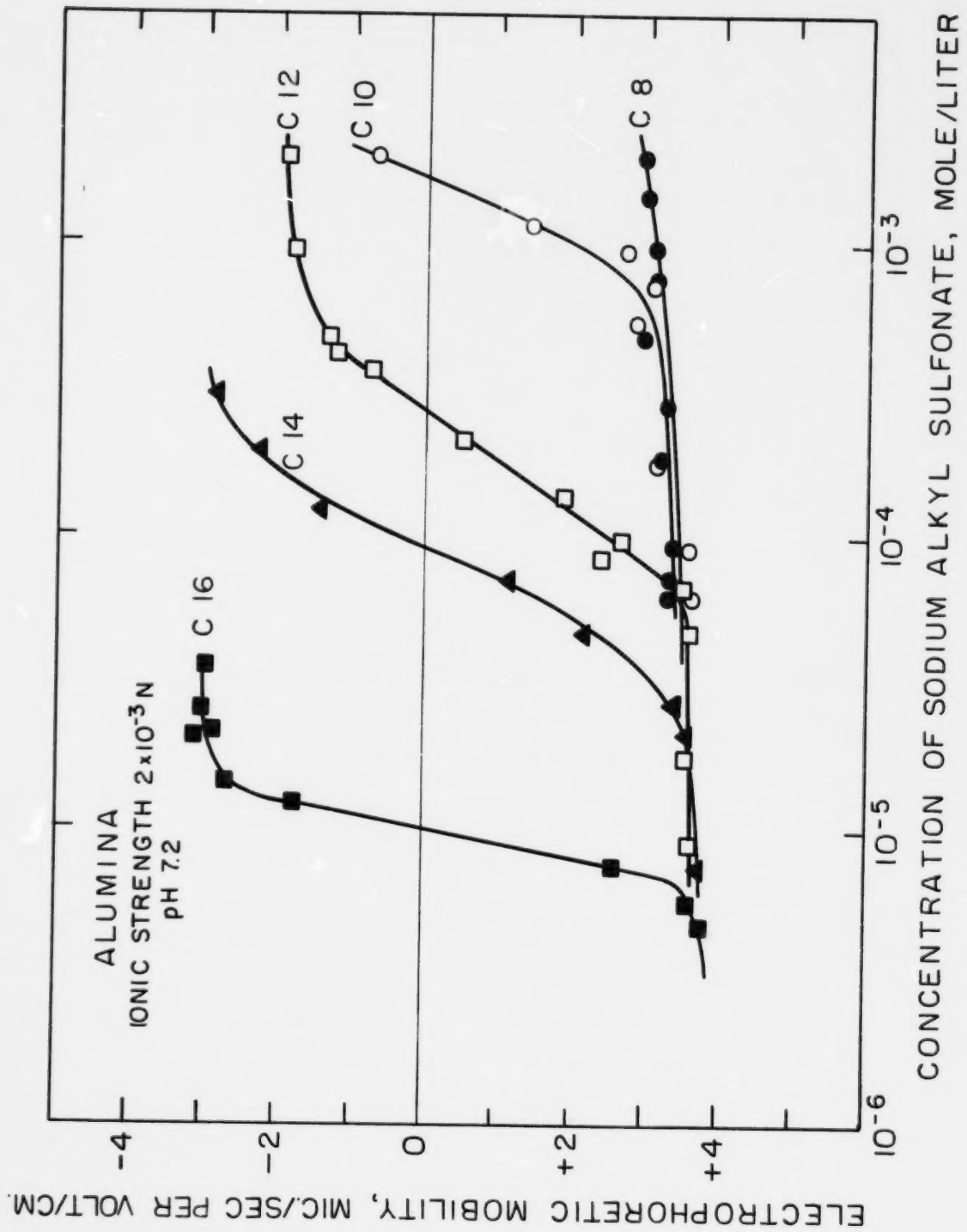
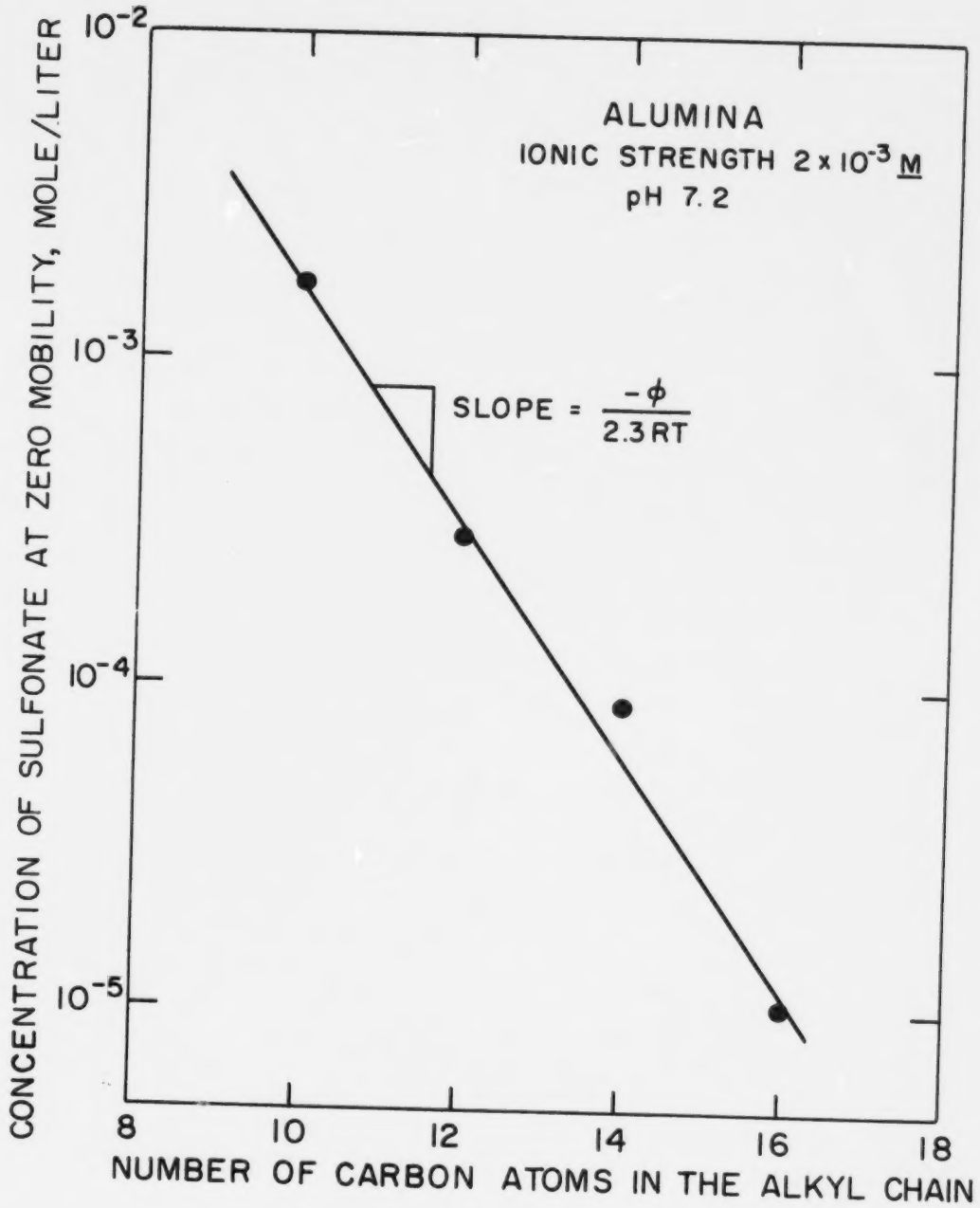

ALUMINA
IONIC STRENGTH 2x10⁻³N
pH 7.2
C 16
C 14
C 12
C 10
C 8
-4
-2
0
+2
+4
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
ELECTROPHORETIC MOBILITY, MIC./SEC PER VOLT/CM.
CONCENTRATION OF SODIUM ALKYL SULFONATE, MOLE/LITER

FIGURE 4


ALUMINA
IONIC STRENGTH 2 x 10⁻³ M
pH 7.2
SLOPE = -φ / 2.3RT
CONCENTRATION OF SULFONATE AT ZERO MOBILITY, MOLE/LITER
10⁻²
10⁻³
10⁻⁴
10⁻⁵
8
10
12
14
16
18
NUMBER OF CARBON ATOMS IN THE ALKYL CHAIN

SECTION 2

THE AGGREGATION OF COLLOIDAL ALUMINA DISPERSIONS BY ADSORBED SURFACTANT IONS

by

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ABSTRACT

The stability ratios of suspensions of α-alumina in aqueous solutions of sodium dodecyl sulfonate at constant ionic strength were determined at pH 6.9 and 7.2 at 25°C and at pH 6.9 at 45°C by measuring the rate of change of turbidity. Measurements of adsorption of surfactant by alumina and of electrophoretic mobilities of alumina particles and the extent of coagulation of the same system gave isotherms of the same general form. This indicates that coagulation in this system results mainly by reduction in diffuse layer potential because of surfactant adsorption. The dependence of surfactant adsorption and coagulation on pH is extremely marked; there is a much lesser dependence on temperature. Stability ratios were also calculated from the electrophoretic mobility data and the variation of the ratios with concentration compared with that evaluated from turbidity measurements.

INTRODUCTION

The stability of aqueous colloidal dispersions in the presence of simple cations and anions is reasonably well described in terms of the theory of Derjaguin and Landau[1] and Verwey and Overbeek[2], modified to account for specific ion effects[3] and the action of hydrated complexes[4]. In contrast, the action of polymeric materials on dispersions is reasonably well understood in terms of a "bridging model"[5, 6] in which polymer bridges unite the particles. Ottewill and Watanabe[7-11] have recently treated the coagulation of dispersions by surfactants solely in terms of double layer effects.

It is the aim of present work to examine the action of anionic surfactants on colloidal dispersions by correlating the stability of the dispersions with surfactant adsorption and the resulting changes in the electrokinetic properties. Understanding of the mechanisms in such systems is of technological importance in processes such as flotation, water pollution control and detergency.

THEORY

At low concentrations surfactant ions adsorb at an oxide-water interface as individual ions and since the adsorption in this stage is well described by Guoy-Chapman diffuse double layer theory the long chain surfactant ion can be considered as a simple ion. For example, the log-log adsorption isotherm for dodecyl sulfonate ion on alumina at constant ionic strength, the isotherm has the expected slope of 1.0[12] where adsorption occurs by ion exchange of counter ions.

As the adsorption density increases, at a certain solution concentration range lateral interaction between adjacent hydrocarbon chains of the adsorbed surfactant ions begins to take place. This bulk concentration has been termed the "hemi-micelle" concentration[12-15] by

analogy to the similar phenomenon in bulk solutions of surfactants. With quartz at neutral pH, the two dimensional interaction of adsorbed alkyl ammonium ions occurs at concentrations some 100-fold less than that required for micelle formation in the bulk solution.

If a surfactant ion acts as a simple ion, it would be expected that in the first adsorption stage prior to hemi-micelle formation, the reduction in diffuse layer charge would result in simple coagulation. When the adsorbed ions associate, we must describe the change in charge and the concomitant change in coagulation in terms of the Stern-Grahame theory[16] of the compact double layer. This can be done by expressing the total energy of interaction, V_t, between the double layers on adjacent solid particles as the sum of the attractive (V_a) and repulsive (V_r) contributions. It is this potential V_t which retards the process of rapid coagulation by a factor W, the stability ratio of Fuchs[1, 2, 7, 17], given by,

$$W = 2a \int_{2a}^{\infty} [\exp(V_t/kT)] \frac{dH}{H^2} \qquad (1)$$

where a is the particle radius, H the distance between the particle centers, k is the Boltzmann constant and T is the absolute temperature. Notice that as W decreases rapid coagulation occurs. A detailed discussion of the significance of the W factor has been given recently[17]. Following the treatment of Ottewill and Watanabe[7-11], the total energy of interaction of double layers, V_t, can be expressed in terms of the Stern potential, ψ_δ, to yield an expression for the stability ratio in terms of ψ_δ, namely,

$$\ln W = \frac{A}{24\,kT} \left[\frac{D^2 \psi_\delta^2}{(1 + 2\kappa a)} - D\psi_\delta \right] - 3/4 \ln (D\psi_\delta)^2 + B \qquad (2)$$

where $$D^2 = \frac{12(2\kappa a + 1)\epsilon a}{A} \quad (3)$$

and $$B = \ln 2\sqrt{\pi} - 1/2 \ln \frac{A}{(6kT)} + \frac{A}{24kT} \quad (4)$$

where A is the Hamaker constant, taken as 10^{-12} ergs for the present system, κ is the Debye-Hückel reciprocal length and ϵ the dielectric constant. As discussed in previous publications[7-13] the electrokinetic potential, ζ, can be evaluated from the electrophoretic mobility of the particles and by approximating ζ for ψ_δ, theoretical values of W for all values of the concentration of surfactant can be calculated from the curve of electrophoretic mobility vs surfactant concentration.

EXPERIMENTAL

The system chosen for the present study was alumina-water-sodium dodecyl sulfonate, described in detail in a previous publication[12]. The radius of the alumina particles are in the range of 10^{-5} cm. All measurements were conducted at 2×10^{-3} M NaCl ionic strength, pH being adjusted with HCl or NaOH. The electrophoresis assembly, adsorption cell, and the methylene blue technique used for determining residual sulfonate are described in the previous publication[12].

The change in coagulation behavior due to adsorbed surfactant was determined using an apparatus consisting of a tube containing the suspension and surrounded by a glass constant-temperature jacket through which is passed a collimated light beam from a tungsten lamp. The attenuation of this light beam by the particles of the suspension is detected with selenium photocell couples to a recorder read-out. The recorder traces the change in light intensity with time due to the coagulation of the suspension and its subsequent sedimentation. In order to express this change in turbidity with time in terms of a parameter which is proportional to the stability ratio, W, it is necessary to obtain the slope of the turbidity-time

curve at zero time. The turbidity, τ, is given by the expression,

$$I = I_o \exp(-\tau L) \tag{5}$$

where I_o and I are the intensities of incident and transmitted light respectively, and L is the optical length of the system. Differentiating Equation (5) with respect to time,

$$\frac{dI}{dt} = I_o(-L)\exp(-\tau L)\frac{d\tau}{dt} \tag{6}$$

τ has the same initial value in all experiments and hence if, as in the present experiment dI/dt is measured as t tends to zero,

$$\frac{d\tau}{dt} = k_1 \frac{dI}{dt} \tag{7}$$

where k_1 is an apparatus constant. The turbidity of the suspension is related to its colloidal stability by the relation[7-11]

$$\tau = Kv^2 N_o \left(1 + \frac{k_o N_o t}{W}\right) \tag{8}$$

where K is an optical constant, v is the volume of the individual particles, N_o is the number of particles initially present per cm^3 and k_o is a constant.

Again differentiating with respect to time,

$$\frac{d\tau}{dt} = \frac{Kv^2 N_o^2 k_o}{W} \tag{9}$$

or from Equations (8) and (10)

$$\frac{1}{W} = k_2 \frac{dI}{dt} \tag{10}$$

where k_2 is a constant for the present system and is given by,

$$k_2 = k_1 / kv^2 N_o^2 k_o \tag{11}$$

We can now compare the experimental values, W_{exp}, determined from the slope of turbidity-time plot of a dispersion of the solid in surfactant solutions with the values, W_{calc}, calculated from electrophoretic data using Equation (2). Provided the action of surfactant ions on the colloidal stability is due simply to reduction of the diffuse layer potential, then the two stability ratios should vary in the same way with changes in surfactant ion concentration.

RESULTS

The experimental stability factor, W_{exp}, for suspensions of alumina in aqueous solutions of sodium dodecyl sulfonate at 25°C and 2×10^{-3} M total ionic strength are given in Figures 1 and 2 for constant pH values of 7.2 and 6.9, respectively, together with the variation of the adsorption density, Γ, and the electrophoretic mobility, μ_e. Notice that for purposes of comparison, W and μ_e are plotted in a decreasing fashion whereas Γ is plotted in an increasing fashion.

The clearly defined three-stage nature of the adsorption process is shown by the numbers 1, 2, and 3 along the isotherm in Figure 1.

In Figure 3 is shown the adsorption and stability isotherms for the same system as shown in Figure 2, but at 45°C. The physical construction of the electrophoresis cell prevented precise measurement of mobilities at temperatures other than 25°C.

Using Equation (2) and the electrophoretic mobility data at 25°C and pH 7.2 and 6.9, curves of W_{calc} were constructed and are shown in Figure 4. No strict theoretical significance should be placed on the magnitude of the W_{calc} or W_{exp} values, since the constants involved in their determination are uncertain. It is clear that for Stage 1 and Stage 2 adsorption, the W_{calc} stability curves of Figure 4 are of the same form as the experimental stability curves of Figures 1 and 2.

However, while the W_{exp} curves follow the adsorption isotherms during Stage 3, the W_{calc} curve during this stage reverses its slope and differs markedly from the experimental curve.

DISCUSSION

Adsorption and Electrokinetic Data

The characteristic feature of the adsorption isotherms of alkyl sulfonates on alumina is the three-stage nature of the isotherm. The three stages, shown in Figure 1 as 1, 2, and 3, respectively, occur at each pH, temperature, and ionic strength studied and the concentrations at which these are changed in the process of adsorption are functions of these three variables. In Table 1 are summarized the solution concentrations that define the process of adsorption of sodium dodecyl sulfonate on alumina.

The adsorption isotherm has been described in detail before[12] and will only be briefly mentioned here. For the alumina-alkyl sulfonate system, the concentration corresponding to transition between Stages 1 and 2; that is, the hemi-micelle concentration, can be seen from Figures 1 and 2 and Table 1, to occur at a lower concentration as the pH decreases. Remembering that the zero point of charge of α-Al_2O_3 is at pH 9.1[18], this decrease in the hemi-micelle concentration with decreasing pH means that the higher surface charge at pH 6.9 ensures that hydrocarbon chain interaction will occur at a lower solution concentration than for the system at pH 7.2. The considerable effect of pH has been shown to continue as the pH is further lowered[12].

The effect of raising the temperature is to displace the whole of the adsorption (and stability) isotherms to a higher solution concentration range. The data suggest that at 45°C the increased mobility or kinetic energy of the adsorbed species tends to inhibit hemi-micelle formation.

Micelle formation in bulk surfactant solutions is similarly affected by an increase in temperature[19]. The interesting comparison can be made between the effect on the adsorption process of either an increase in temperature or an increase in pH; the data show that a pH increase of only 0.3 has a far greater effect on surfactant adsorption than a 20°C increase in temperature. We may conclude that sulfonate adsorption on alumina is primarily physical (i.e., simple electrostatic). If adsorption is primarily electrostatic, surface charge, controlled by the pH, will have a large effect. For low activation energies of adsorption, temperature change has a minor effect.

Stability Data

The close similarity between the adsorption, electrokinetic, and experimental stability isotherms as presented in Figures 1, 2, and 3 is an indication that the coagulation process here is analogous to that by simple ion adsorption to reduce the diffuse layer potential. It is only when the data are presented as in Figure 4 that it becomes apparent that the total aggregation process is not simple coagulation.

At low surface coverages and on either side of the hemi-micelle concentration both stability isotherms are of the same form as the adsorption and electrokinetic isotherms. At low surface coverage also, a decrease in stability ratio is observed probably due to the slight decrease in the electrophoretic mobility in this range as shown in Figure 1. In fact the actual decrease in electrophoretic mobility in this region might be higher than that observed in the experiments, since surface conductance probably masks the effect of small additions of electrolytes such as the sulfonate used here. When hemi-micelle formation begins adsorption is enhanced and the adsorption, electrokinetic, and stability isotherms all show the increased slope expected from the more extensive adsorption.

When the surface charge is reduced to zero and becomes negative, the alumina should begin to disperse. This is shown in Figure 4 as a minimum in W_{calc} at the concentration at which the mobility reaches zero. The experimental stability curves of Figures 1, 2, and 3, however, do not show redispersion, but indicate, in contrast, more extensive aggregation after the point of zero mobility. Experimentally, it was observed that many finer particles still remained positively charged. Aggregation of the colloidal particles could continue to occur because of the phenomenon of mutual coagulation. It should be noted that we observed qualitatively that the system showed a tendency to redisperse again at much higher concentrations than that shown in Figures 1 and 2.

This raises the question whether in Stage 3 at least the aggregation is due to simple coagulation. The assumption that change in the stability of colloids due to adsorbed surfactant ions can be treated in terms of simple ion adsorption would appear to be unwarranted.

An explanation, and one of considerable interest, is that it may be possible for particles with high surface coverage to come together to further reduce their surface energies, the adsorbed surfactant molecules essentially bridging the particles together. Along a line of centers between two particles aggregated in this way we would have particle-adsorbed surfactant-adsorbed surfactant-particle. Such an aggregation would tend to remove some of the hydrocarbon chains of adsorbed surfactant molecules out of an aqueous environment and thereby lower the free energy of the system.

In the sense that these aggregates involve surfactant bridges, aggregation during Stage 3 adsorption might be referred to as flocculation[5, 7] rather than simple coagulation. In such a case the work of adsorption, w_δ, for ions adsorbed into the Stern plane will be as follows for each stage of the adsorption process:

STAGE 1: $$(w_\delta)_1 = zF\psi_\delta \qquad (13a)$$

where z is the valence of surfactant ion, F is the Faraday constant, and ψ_δ is the potential at plane δ .

STAGE 2: $$(w_\delta)_2 = zF\psi_\delta + n\phi \qquad (13b)$$

where ϕ is van der Waals' cohesive energy associated with removal of one mole of CH_2 groups from an aqueous environment and n is the effective number of moles of CH_2 groups that have been removed from water per mole of electrolyte due to hemi-micelle association.

STAGE 3: $$(w_\delta)_3 = zF\psi_\delta + n\phi + (N-n)\phi \qquad (13c)$$

where N is the total number of CH_2 and CH_3 groups in the surfactant molecule. $(N-n)\phi$ thus represents the added energy which can be gained by the system due to surfactant molecular bridges. Despite the recent experimental study[12], we cannot completely rule out the possibility of chemisorption or specific interaction of sulfonate ions with ions in the alumina lattice. If chemisorption occurs we must add a further adsorption potential in Equations (13a), (13b), and (13c).

SUMMARY

The stability ratios for alumina dispersions in sodium dodecyl sulfonate solutions were determined at pH 6.9 and 7.2 at 25°C and at pH 6.9 at 45°C by measuring the rate of change of turbidity. Measurements of adsorption of surfactant by alumina and of the electrophoretic mobility of alumina particles were carried out for the same system. Close similarity among the various observed isotherms indicates that the coagulation resulted mainly by the reduction of double layer potential due to surfactant adsorption. Stability ratios were also calculated from the electrophoretic mobility data and compared with those evaluated from turbidity measurements. In general, good agreement was found

between the observed and calculated values up to the concentration of surfactant where the mobility is reduced to zero. There is then divergence of the observed coagulation from that calculated from double layer theory indicating that other mechanisms can contribute to coagulation.

ACKNOWLEDGMENTS

The authors wish to acknowledge the National Institute of Health (Grant No. WP-00692-01) for support of this research.

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TABLE 1

Summary of Critical Concentrations for Sodium Dodecyl Sulfonate Adsorption on Alumina

Critical Concentration	From Adsorption and Electrokinetic Data			From Stability Data		
	pH 7.2 25°C	pH 6.9 25°C	pH 6.9 45°C	pH 7.2 25°C	pH 6.9 25°C	pH 6.9 45°C
Hemi-micelle concentration (C_{HM} mole/l) x 10^5	8.5	3.3	5.0	8.5	5.5 (approx)	7.0 (approx)
Concentration at zero mobility ($C_{\mu_e = 0}$ mole/l) x 10^5	35	30	-	-	-	-
Concentration at Stage 2 to 3 transition (C_{2-3} mole/l) x 10^5	30	20	24	35 (approx)	20 (approx)	22 (approx)

FIGURE CAPTIONS

Figure 1: Adsorption, electrophoretic mobility, and colloidal stability isotherms for α-alumina at pH 7.2, 2×10^{-3} M ionic strength and 25°C as a function of the equilibrium concentration of sodium dodecyl sulfonate.

Figure 2: Adsorption, electrophoretic mobility, and colloidal stability isotherms for α-alumina at pH 6.9, 2×10^{-3} M ionic strength and 25°C as a function of the equilibrium concentration of sodium dodecyl sulfonate.

Figure 3: Adsorption and colloidal stability isotherms for α-alumina at pH 6.9, 2×10^{-3} M ionic strength and 45°C as a function of the equilibrium concentration of sodium dodecyl sulfonate.

Figure 4: Colloidal stability isotherms calculated from mobility data for α-alumina at 25°C and 2×10^{-3} M ionic strength at pH 7.2 and 6.9 as a function of the concentration of sodium dodecyl sulfonate.

FIGURE 1

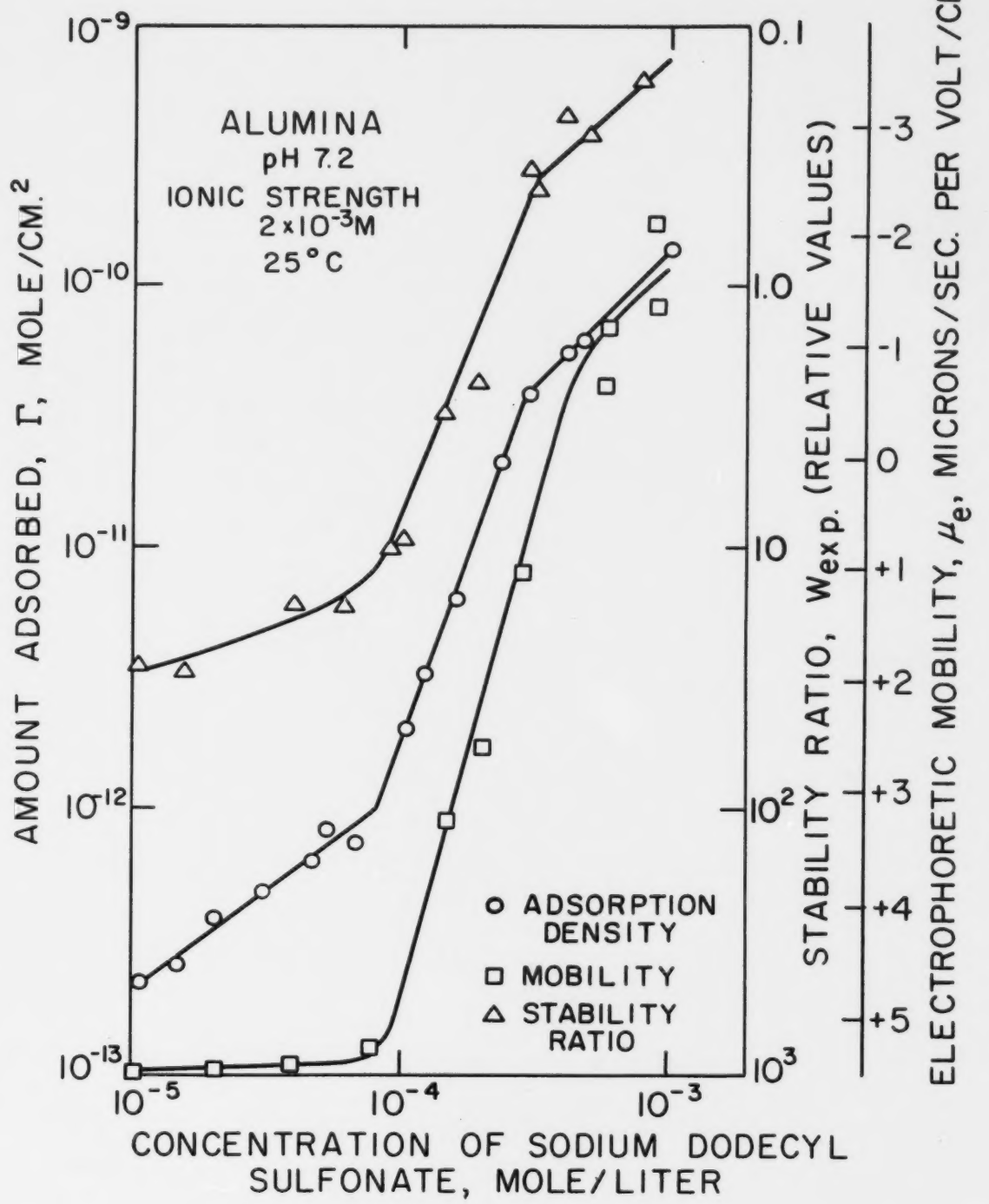

ALUMINA
pH 7.2
IONIC STRENGTH
2×10⁻³M
25°C
AMOUNT ADSORBED, Γ, MOLE/CM.²
STABILITY RATIO, W exp. (RELATIVE VALUES)
ELECTROPHORETIC MOBILITY, μe, MICRONS/SEC. PER VOLT/CM.
ADSORPTION DENSITY
MOBILITY
STABILITY RATIO
CONCENTRATION OF SODIUM DODECYL SULFONATE, MOLE/LITER

FIGURE 2

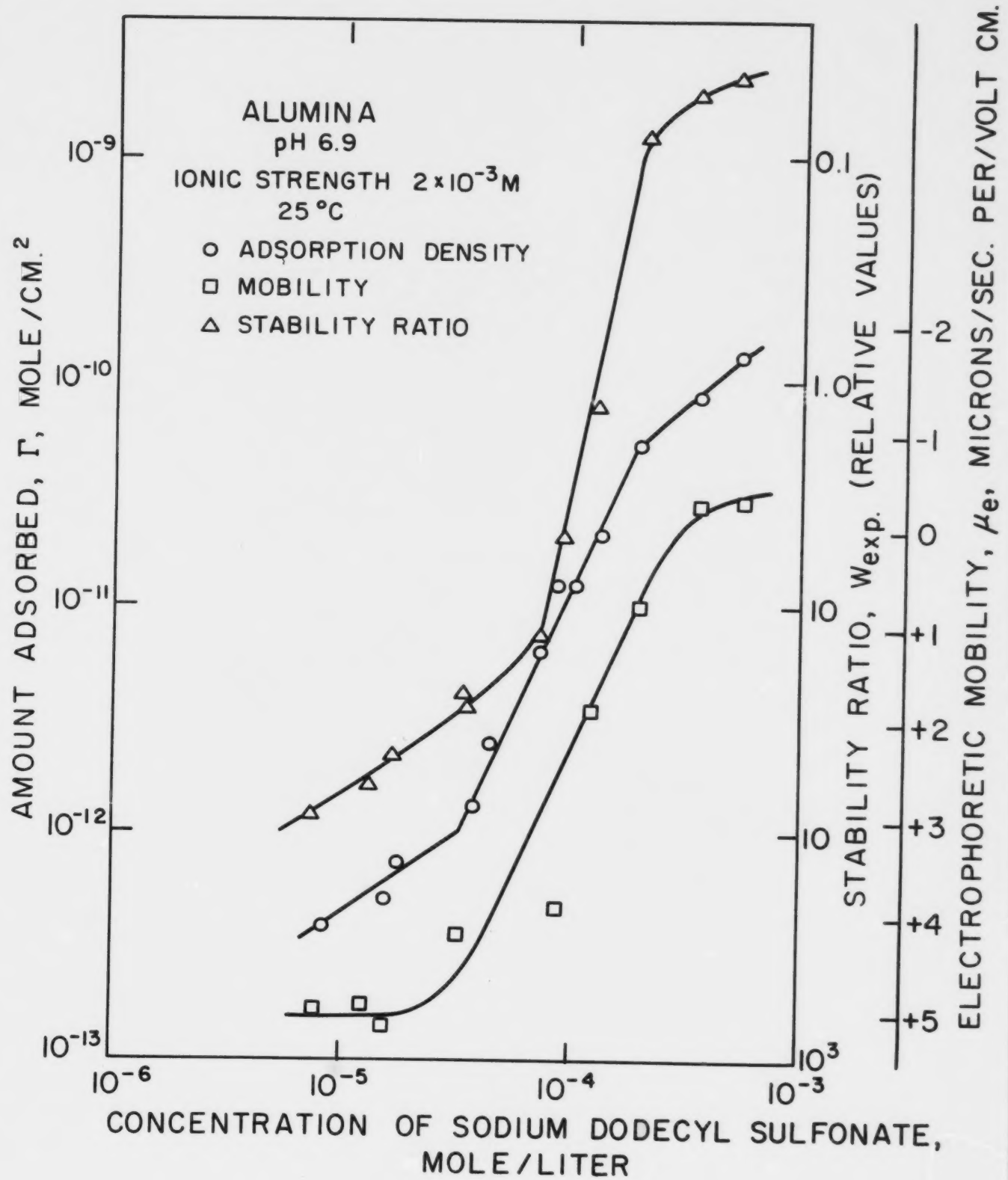

ALUMINA
pH 6.9
IONIC STRENGTH 2×10⁻³M
25 °C
ADSORPTION DENSITY
MOBILITY
STABILITY RATIO
AMOUNT ADSORBED, Γ, MOLE/CM.²
STABILITY RATIO, Wexp. (RELATIVE VALUES)
ELECTROPHORETIC MOBILITY, μe, MICRONS/SEC. PER/VOLT CM.
CONCENTRATION OF SODIUM DODECYL SULFONATE, MOLE/LITER

FIGURE 3

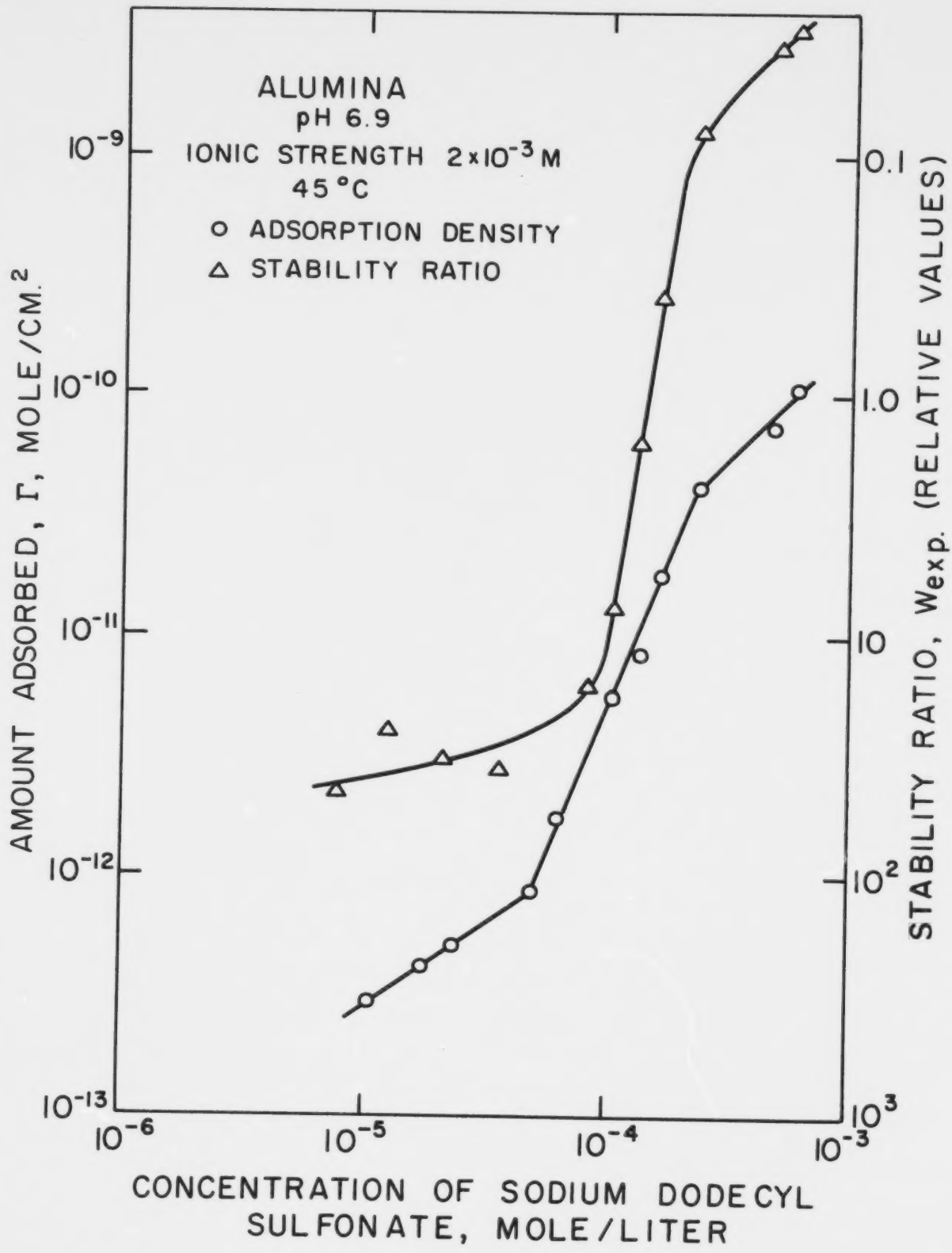
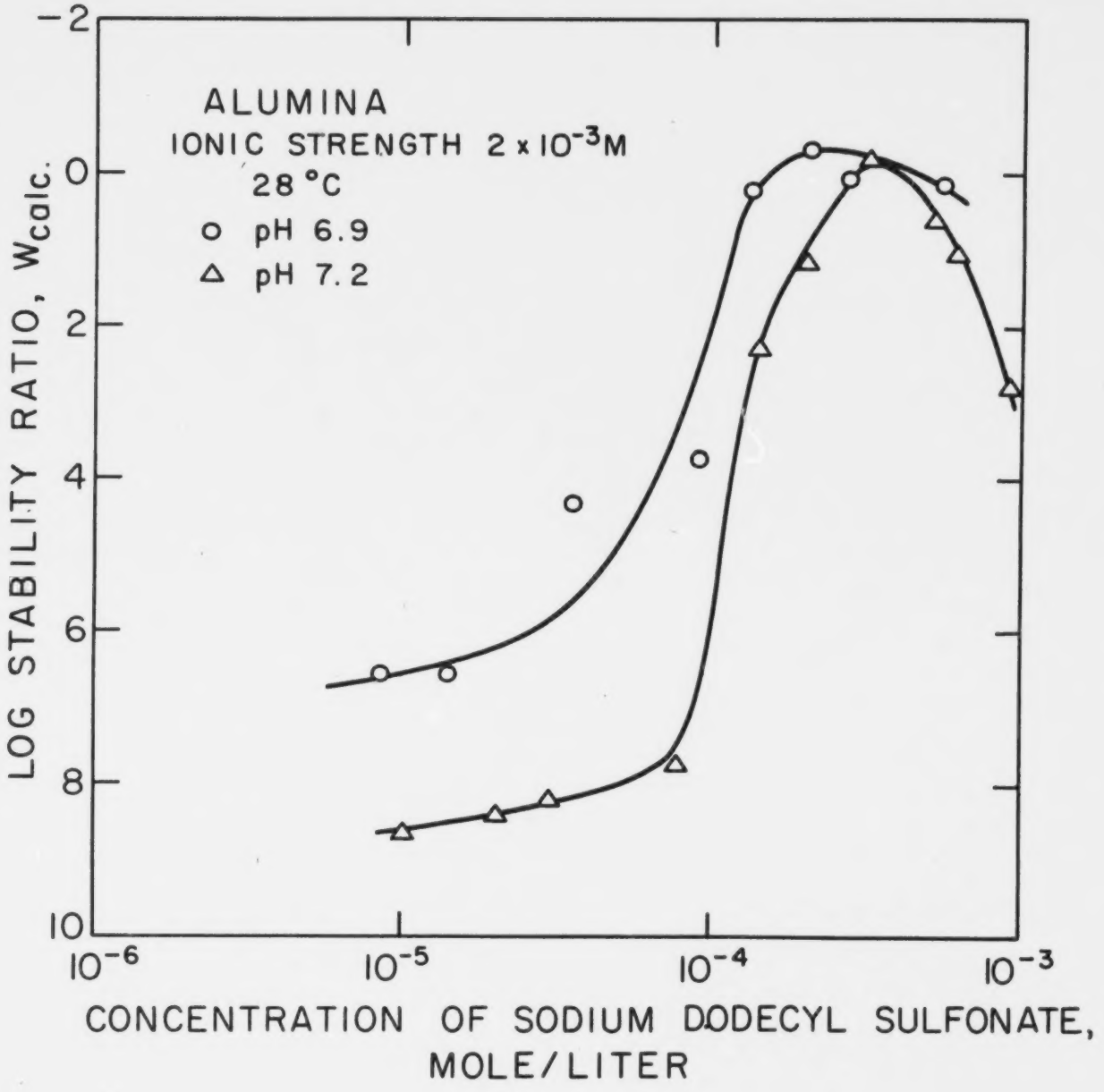

ALUMINA
pH 6.9
IONIC STRENGTH 2×10⁻³ M
45 °C
o ADSORPTION DENSITY
Δ STABILITY RATIO
AMOUNT ADSORBED, Γ, MOLE/CM.²
STABILITY RATIO, Wexp. (RELATIVE VALUES)
CONCENTRATION OF SODIUM DODECYL SULFONATE, MOLE/LITER
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
0.1
1.0
10
10²
10³
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³

FIGURE 4


ALUMINA
IONIC STRENGTH 2 x 10⁻³M
28 °C
o pH 6.9
Δ pH 7.2
LOG STABILITY RATIO, Wcalc.
-2
0
2
4
6
8
10
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
CONCENTRATION OF SODIUM DODECYL SULFONATE, MOLE/LITER

SECTION 3

THE HEAT OF IMMERSION OF ALUMINA INTO AQUEOUS SODIUM DODECYL SULFONATE SOLUTIONS

by

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ABSTRACT

The heat of immersion of α-alumina was measured in water and in aqueous solutions of sodium chloride and sodium dodecyl sulfonate at various pH values. In sodium chloride solutions without detergent, the heat of immersion of alumina was found to be the same as that in distilled water at the same pH. In alkaline solutions, $-\Delta h_I$ decreased slightly. Only below the zero point of charge of alumina, i. e. below pH 9. 1, do sulfonate ions affect the heat of immersion of alumina. As increased adsorption occurs either through increasing the detergent concentration in the bulk solution or by lowering the pH, the sensible heat evolved upon immersing alumina; increases, reaching a maximum at monolayer coverage. A model for the adsorption of sulfonate ions onto a hydrated surface of alumina is presented.

The adsorption of ionic detergents at solid-water interfaces is of great importance in such broad fields as detergency, water rennovation, mineral flotation. and corrosion inhibition. In order to study details of how organic surfactants adsorb at solid-water interfaces, various researchers have extensively used a variety of experimental techniques including measurement of adsorption isotherms, electrokinetic potentials, contact angles, stability of suspensions, and flotation behavior. Thus far, immersional heat measurements have never been used for investigation of the adsorption of ionic detergents from aqueous solutions at the surface of polar solids. However, Mellgren[1], has recently published the results of a study of the heat of adsorption of potassium ethyl xanthate at the surface of galena (lead sulfide) using immersional calorimetry to determine heats of adsorption. Mellgren found that xanthate is strongly chemisorbed by lead sulfide.

The present investigation is concerned with the adsorption of sodium dodecyl sulfonate at the alumina-water interface, a system in which the surfactant adsorbs as counter ions in the electrical double layer[2]. By measurements of adsorption isotherms together with electrophoretic mobilities, it was found that sulfonate adsorption is extremely pH sensitive and that adsorption occurs only when the surface of the solid is positively charged. The objective of this investigation has been to extend our study of this adsorption process by carrying out measurements of the heat of immersion of alumina into aqueous sodium dodecyl sulfonate solutions in conjunction with determination of adsorption isotherms. Specifically, one of our purposes has been to ascertain the feasibility of using calorimetric techniques for study of adsorption in systems where double layer properties control the adsorption process.

EXPERIMENTAL

Materials

Alpha-alumina (Linde "A" alumina) of 99.95 percent purity was used throughout the experiments[2]. The surface area of this material, as measured

by B.E.T. gas adsorption, is 15 m^2/gm.

The sodium dodecyl sulfonate (SDS) used for these experiments was prepared from high purity dodecyl sulfonic acid by neutralization with sodium hydroxide, and the resulting sodium salt was purified by recrystallization from hot absolute ethyl alcohol. All solutions used in this study were made from conductivity water.

The Calorimeter

The calorimeter used for measurements of heats of immersion, as presented schematically in Figure 1, consists of a 1000-cc silvered Dewar, with a glass pin at the bottom of the Dewar for breaking the bulb containing the outgassed sample. The sample bulb was designed similarly to that described by Hackerman[3], except that the thin break-off seal at the bottom of the bulb was larger so that the powder could readily be dispersed into the solution inside the Dewar. The sample bulb, which was rotated at 100 rpm, was used as the stirrer; there was no measurable heat effect due to the breakage of the bulb.

The temperature change of the calorimeter was measured by a 100,000-ohm Fenwal thermistor, which was immersed inside the Dewar in a glass tube, the end of which was a thin bulb containing oil. Heat transfer from the calorimeter to the thermistor was found to be rapid. The change of the resistance of the thermistor was measured by the AC bridge circuit described by La Force et. al.[4]. The heat capacity of the calorimeter was determined in terms of the change of resistance of the thermistor by putting in a known amount of heat through a carbon resistance heater immersed in oil. Both the current passing through a precision 200-ohm resistance and the voltage drop across the heater resistance was measured simultaneously during the course of the calibration. The heat capacity of the calorimeter was determined on several occasions before and after breakage of the bulb, and these measurements agreed very well with each other. For most runs, the heat capacity was determined after the breakage of the bulb. Since sulfonate ions do not adsorb on glass from aqueous solution, the all-glass construction of the calorimeter was ideal for this adsorption system.

Experimental Procedures

All of the samples of alumina were outgassed at 300°C for 24 to 48 hours at pressures of 5×10^{-5} mm of Hg in Pyrex sample bulbs. Outgassing for times longer than 24 hours had no effect on the results. After outgassing, the sample bulbs were vacuum sealed at the outgassing temperature.

After loading, the calorimeter was equilibrated overnight. For each run, before the breakage of the bulb an initial steady drift rate was established for a time period of about 7 to 10 minutes. Subsequently, the stirring mechanism together with the sample bulb was lowered about 1/2 inch in order to break the end of the bulb against the pin at the bottom of the calorimeter. The change of temperature was continuously measured until a final steady state was attained, this usually being about five to ten minutes. In most cases the initial and final steady state drift rates were similar, since the change of the temperature of the calorimeter was very small and hence no heat transfer correction was necessary; in cases where drift rates were not identical, a correction was made graphically. The rate and magnitude of the heat input to the calorimeter for calibration purposes, were kept similar to that of the actual run, in order to minimize the uncertainty due to the heat loss correction, as they will tend to cancel each other. Typical temperature changes were 0.01 to 0.025°C. The measurements were carried out at room temperature, 23°C; and since the stirrer, thermistor, heater, and the bath were at the same temperature the results were quite reproducible. The estimated uncertainty of the measurements is about 2 percent.

To find out whether the ratio of sample wieght to solution volume had any effect on the measured heat effects, the sample size was varied from 4 to 15 grams and the water volume from 700 to 900 cc. No dependence of this nature was observed. In our experiments, usually 10 grams of solids were immersed into 850 cc of solution.

Most of the experiments to study the pH dependence of the heat of immersion were carried out by breaking the sample bulbs in solutions containing

2×10^{-3} M NaCl . The pH of the solutions was measured after each run. A series of experiments was run to compare the heat of immersion of alumina into water and into the NaCl solutions, and no effects due to the presence of NaCl were observed. Representative experimental data are given in Table 1 to illustrate effects due to NaCl and HCl or NaOH used for pH adjustment.

Table 1. The effect of NaCl and pH on measurement of heats of immersion.

Final pH	NaCl Conc., M/l	Heat of Immersion ergs/cm^2	Time for heat evolution, min.
4.90	10^{-3}	-860	3
4.73	2×10^{-4}	-867	2.5
4.80	0	-859	3.5
6.85	10^{-2}	-854	3
7.05	10^{-3}	-834	3
6.50	0	-836	3
7.60	0	-840	5
6.40	10^{-3}	-849	4.5
9.80	0	-820	4
9.18	10^{-3}	-817	3
8.85	0	-819	3
8.53	0	-813	2

Experiments with Sodium Dodecyl Sulfonate

In the research concerned with the adsorption of SDS, alumina was immersed into solutions containing SDS and 2×10^{-3} M NaCl for ionic strength control. Measurements were carried out at constant pH and also over a pH range at constant sulfonate equilibrium concentration. One essential difference between determination of the heats of immersion of alumina in water and in the sodium dodecyl sulfonate solutions was that in the surfactant solutions about

5 to 10 minutes was required for total heat evolution whereas about 3 to 5 minutes was required in water. Figure 2 presents typical runs on the rate of heat evolution for immersion of alumina into water and into aqueous solutions containing NaCl and SDS . The rate of adsorption, as monitored by the rate of heat evolution, is dependent upon the amount of material adsorbed and on the rate of stirring (it was impossible to have absolutely identical stirring conditions because the geometry of the sample bulb was not exactly the same for each run). In all cases, the runs were monitored for up to one hour, and it was found that usually within 10 minutes after breakage of the bulb most of the sensible heat was evolved.

In one series of experiments, the pH was maintained constant at pH 3.5 with the sulfonate concentration being varied. This value of the pH was selected because the adsorption density of sulfonate ions is large due to the high positive surface charge. Furthermore, the extent of adsorption is not so sensitive to pH as at higher pH values[2]. At this lower pH value it was much less difficult to maintain a constant pH value without adding undesired buffers, and even under these conditions, the pH could be maintained only within $\pm$ 0.2 pH unit. It was also observed that the rate of adsorption of sulfonate ions was much more rapid at this lower pH range, which improved the accuracy of the calorimetric measurements. Another series of runs were made to determine the effect of pH on the heats of adsorption at constant equilibrium bulk concentration. It was found to be quite difficult to maintain a constant final equilibrium sulfonate concentration and accordingly the SDS concentration was $2.5 \pm 1.5 \times 10^{-4}$ M .

After each run the final concentration of the sulfonate was determined by methylene blue method[2, 5]. From the initial and final concentration of the sulfonate ions and the known weight of alumina, the adsorption isotherms were determined.

EXPERIMENTAL RESULTS

Effect of pH

The heats of immersion of alumina outgassed at 300°C are given as part of Figure 6 as a function of pH in 2×10^{-3} M NaCl at 23°C. Up to about pH 6

or 7, the heat of immersion is constant at about -850 ergs/cm^2 with decreasing acidity. Above pH 7, there is a slight decrease in the heat of immersion. The uncertainty of the results is about 15 ergs/cm^2.

Effect of Sodium Dodecyl Sulfonate at pH 3.5

At pH 3.5 ± 0.2 and 2 x 10^{-3} M NaCl, the adsorption of sodium dodecyl sulfonate by alumina was determined at 23°C. Figure 3 presents the amount of dodecyl sulfonate adsorbed versus the equilibrium concentration of SDS in solution. These data were obtained by analysis of the solutions after carrying out heat of immersion experiments. This figure shows that a plateau is reached at monolayer coverage (5 x 10^{-10} mole/cm^2) and that multilayer adsorption occurs at still higher concentrations of SDS. From these experimental results, the heat of immersion of alumina into aqueous solutions containing SDS at pH 3.5 is plotted in Figure 4 as a function of the amount of dodecyl sulfonate adsorbed. This figure shows that as the coverage exceeds 10^{-12} mole /cm^2, $-\Delta h_I$ increases, reaching a maximum at a coverage of about 5 x 10^{-10} mole/cm^2.

Effect of pH at Constant SDS Concentration

Figure 5 illustrates how the adsorption density of SDS on alumina varies with pH at an equilibrium concentration of 2.5 ± 1.5 x 10^{-4} M in 2 x 10^{-3} M NaCl at 23°C. This figure shows that as the zero-point-of-charge of alumina (pH 9.1) is approached, adsorption of dodecyl sulfonate ions decreases markedly. On the other hand, lowering the pH causes the amount of adsorption to increase, reaching a monolayer at about pH 3.5. Again, these data were obtained by analyzing the aqueous solution after completion of the calorimetric immersion measurements. In Figure 6, the heat of immersion of alumina at 23°C into solutions whose final SDS concentration was 2.5 ± 1.5 x 10^{-4} M in 2 x 10^{-3} M NaCl is plotted as a function of pH. Observation of this figure shows that the presence of SDS affects the heat of immersion only as the pH is lowered below the zpc of alumina.

DISCUSSION

Our value for the heat of immersion of alumina into water agrees quite well with previous measurements by Wade and Hackerman[3] for similar conditions. In runs with NaCl present there was no detectable difference in the heat of immersion as compared to runs with conductivity water. An important feature of the present results is that the heats of immersion stay fairly constant at a value of -850 ergs/cm^2 from pH 3 to pH 6. Above pH 6 the heats seem to become only slightly less negative. At lower pH, the more exothermic heats might at first hand be considered to be due to some dissolution process, the amount of which remains constant over a range of 3.5 pH units; but this is unlikely. Secondly, for all the runs it took about the same amount of time for the completion of the evolution of the sensible heat, which indicates that if there were any significant dissolution occurring during the run, its rate is not changing with variation of pH. By means of atomic absorption spectrophotometry, analysis of aqueous suspensions of Line "A" alumina showed no detectable aluminum in solution. The important point of these measurements is that pH and NaCl have very limited effect on the heat of immersion by themselves.

At pH 3.5, alumina has a high, positive surface charge with anions functioning as counter ions in the electrical double layer. Under these conditions, alkyl sulfonate ions adsorb as counter ions through electrostatic interaction with the positively charged alumina surface. At higher coverage, the hydrocarbon chains of the adsorbed sulfonate ions associate thereby partially removing themselves from their aqueous environment. The free energy of association of the alkyl chains at the solid-water interface is the same as that for association in bulk solution, or for micelle formation[6].

In our experiments where alumina was immersed into solutions containing 2 x 10^{-3} M NaCl and various amounts of SDS, adsorption of dodecyl sulfate at lower coverages would be analogous to immersion into NaCl solutions except that ion exchange of detergent ions with chloride ions would occur

in the double layer. Most of the counter ions under these conditions occupy the diffuse part of the double layer. As can be seen in Table 1, the measurable heat effects due to the electrical double layer are very slight. Thus, the enthalpy for the exchange of one kind of counter ion (dodecyl sulfonate) for another (chloride) in the double layer therefore would also be expected to be small. On the other hand, as the amount of detergent ions adsorbed in the Stern plane increases, they begin to associate at the surface and this added adsorption potential gives rise to high adsorption densities in the Stern plane. Previous work showed that the adsorption density must exceed 10^{-12} mole per cm^2 for the adsorbed surfactant ions to begin to associate[2]. Figure 4 shows that the heat of immersion of alumina begins to increase from -850 ergs per cm^2 as the adsorption density exceeds 10^{-12} mole per cm^2, reaching a value of about -1100 ergs per cm^2 at monolayer coverage, about 5×10^{-10} mole per cm^2. At still higher adsorption densities, the heat of immersion remains approximately constant.

Before considering the various contributions to the heat of immersion of alumina into aqueous solutions of sodium dodecyl sulfonate, let us briefly review the analysis by Skewis and Zettlemoyer[7] of the heat of wetting of Graphon into aqueous sodium dodecyl sulfate solutions. They considered the heat of immersion to be a replacement of the surface enthalpy of the solid by interfacial enthalpies arising from the adsorption of solvent and solute. In their system, they suggested that the total heat of immersion would be determined by the heat of dilution due to the decrease in detergent concentration resulting from adsorption, the heat of demicellization of the detergent in solution, the replacement of the enthalpy of the solid-vacuum surface by the surface enthalpy of Graphon with adsorbed detergent and the surface enthalpy of Graphon with adsorbed water, together with the surface enthalpy of the adsorbed species in contact with solution.

In analyzing our experimental data, it should be pointed out that several marked differences exist between the adsorption systems involving detergent-water-Graphon and detergent-water-alumina. There is weak inter-

action between water molecules and the nonpolar Graphon surface; there is very strong interaction between water and an oxide surface. The heat of adsorption of water on alumina[8] is nearly an order of magnitude larger than for Graphon. Oxides have a high surface charge that results from surface reaction with hydrogen and hydroxyl ions, whereas Graphon would bear a very low surface charge, probably due to any oxygenated sites that may be present. As a result, detergent ions adsorb onto such a nonpolar surface as Graphon because their hydrocarbon chains replace water at the surface, in contrast to the electrostatic forces that give rise to the adsorption of the detergent anions on the positively charged alumina. Thus, on Graphon the charged heads of the detergent ions would orient away from the solid, but on alumina they would orient toward the solid (at least below monolayer coverage). Above the monolayer, the additional detergent ions would adsorb only through interaction with the hydrocarbon chains of the first layer of adsorbed ions and the charged heads then would orient away from the surface. The buildup of a second layer of adsorbed sulfonate ions on alumina would then be energetically almost identical to the formation of micelles in bulk solution.

In the experiments presented in this paper, the starting concentration of SDS never exceeded 0.002 M, which is considerably below the cmc. Since the heat of dilution of the quite dilute solutions used in this investigation are negligibly small, effects due to the heat of dilution and heat of micellization in the solution do not appear in the heat of immersion.

There is no evidence for chemisorption of sulfonate ions on alumina; adsorption of sulfonate ions results only when the surface of the solid is positively charged, that is below pH 9. Because of the strong interaction of oxides with water molecules, it seems probable that the first layer of adsorbed water molecules may not be desorbed from alumina with the adsorption of the dodecyl sulfonate ions. Figure 4 shows that as the adsorption density exceeds the surface concentration where appreciable adsorption in the Stern layer begins to occur, $-\Delta h_I$ begins to increase over the value

otained for pH 3.5 and NaCl without detergent (the same value as obtained for immersion into water). Our model is that upon immersing alumina into a detergent solution, a water-alumina interface is first created with the generation of a positive surface charge, followed by the adsorption of chloride and dodecyl sulfonate ions as counter ions. Only those ions adsorbed into the Stern layer affect the heat of adsorption; heat effects due to counter ions in the diffuse part of the double layer must be negligibly small. Now as sulfonate ions begin to adsorb into the Stern layer due to the interaction of their hydrocarbon chains, a layer of water molecules remains between the sulfonate head and the solid surface. Smolders[9] found that decyl sulfonate ions are hydrated when they adsorb at the mercury-water interface. Additional evidence of adsorption with a layer of solvent molecules between the solid and the ions adsorbed into the Stern layer is demonstrated by the investigation of Mackor[10] on the adsorption of alkaline earth cations on silver iodide.

Because we do not know the orientation of the adsorbed detergent ions at various coverages below the monolayer nor the site-energy distribution, let us consider the process at monolayer coverage and at higher coverages. At monolayer coverage, the immersion process would be governed by the following relation:

$$\Delta h_I = \Delta h_{sw} + \Delta h_{swd} + \Delta h_{d\sigma}$$

where Δh_{sw} is the enthalpy change for the adsorption of a layer of water molecules onto the alumina surface, Δh_{swd} is the enthalpy for the adsorption of a monolayer of detergent ions onto the hydrated surface (which would replace the second layer of water molecules adsorbed at the water-solvent interface), and $\Delta h_{d\sigma}$ is the enthalpy for the formation of the interface between the adsorbed detergent and the aqueous solution. Electrical effects in the double layer are minor, as shown by Table 1. Since the interaction between water molecules in the bulk liquid is about the same as that between

adsorbed water and the second layer[11], the heat of immersion of alumina into water approximately yields a value for Δh_{sw} = -850 ergs/cm^2, and the heat of immersion at monolayer coverage yields an integral heat of adsorption at monolayer coverage of 12 kcal/mole.

Observation of Figure 4 shows that as the adsorption density increases above monolayer coverage the heat of immersion remains nearly constant. If the buildup of multilayers is analogous to the process of micelle formation in bulk solution, then the heat of adsorption beyond monolayer coverage with SDS may be expected to be negligibly small since the enthalpy for micelle formation with sodium dodecyl sulfate is only 0 ± 1 Kcal/mole[12].

Figure 5 shows that the adsorption of dodecyl sulfonate ions falls off sharply as the zpc (pH 9.1) of alumina is approached. As the pH is lowered the adsorption density of detergent ions increases and approaches monolayer coverage at pH 3.5 in solutions containing 2.5×10^{-4} M SDS. Figures 5 and 6 show that heat is begun to be evolved when the adsorption density exceeds 10^{-12} mole/cm^2 and that the heat of immersion reaches a maximum of -1100 ergs/cm^2 at pH 3.5 when monolayer coverage is again reached.

SUMMARY

The heat of immersion in water at 23°C of alumina outgassed at 300° and 5×10^{-5} mm Hg pressure has been found to be -850 ± 20 ergs/cm^2. A series of experiments were run in which the alumina was immersed in 2×10^{-3} M NaCl at various pH values, and the heat of immersion was found to be -850 ergs per cm^2 between pH 3 and about 7, decreasing to about -820 ergs/cm^2 as the solution became alkaline.

The heat of immersion of alumina in solutions containing the same final equilibrium concentration of SDS is the same as that in the absence of SDS at pH 9 and above. However, as the pH is reduced below 9, the heat of immersion becomes more negative, attaining a value of -1100 ergs/cm^2 at pH 3.5. Measurement of the amount of sulfonate ions adsorbed showed that the adsorption is nil above pH 9 and markedly increases as the pH is reduced, at-

taining monolayer coverage at pH 3.5. At pH 3.5, the heat of immersion was measured as a function of the concentration of SDS; and as the sulfonate ions began to adsorb into the Stern layer, the heat of immersion began to become more negative, attaining a value of -1100 ergs/cm^2 at monolayer coverage. At higher coverages, as shown by the adsorption density and calorimetric measurements, the heat of immersion remained at about -1100 ergs/cm^2. No measurable heat effects can be detected when the sulfonate ions occur only in the diffuse part of the double layer.

A model is presented wherein adsorption, once the sulfonate ions begin to associate and adsorb into the Stern layer, occurs by a process where a layer of water molecules exist between the solid surface and the adsorbed layer of sulfonate ions. By this model, an integral heat of adsorption at monolayer coverage is estimated to be 12 kcal/mole. At multilayer coverages, the adsorption process must be nearly identical to micelle formation, with a very low heat of adsorption for the additonal layers, similar to the small enthalpy of micelle formation in bulk solution.

ACKNOWLEDGMENTS

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LIST OF FIGURES

Figure 1. Schematic diagram of the calorimeter.

Figure 2. Rate of heat evolution in the calorimeter.

Figure 3. The amount of dodecyl sulfonate adsorbed at 23°C by alumina as a function of SDS concentration in aqueous solutions containing 2×10^{-3} M NaCl at pH 3.5 ± 0.2.

Figure 4. The heat of immersion of alumina at 23°C as a function of the amount of dodecyl sulfonate ions adsorbed from solutions containing 2×10^{-3} M NaCl at pH 3.5 ± 0.2.

Figure 5. The amount of dodecyl sulfonate adsorbed by alumina at 23°C as a function of pH from solutions containing 2×10^{-3} M NaCl and $2.5 \pm 1.5 \times 10^{-4}$ M SDS.

Figure 6. The heat of immersion of alumina at 23°C as a function of pH in solutions containing 2×10^{-3} M NaCl and in solutions containing 2×10^{-3} M NaCl and $2.5 \pm 1.5 \times 10^{-4}$ M SDS.

FIGURE 1

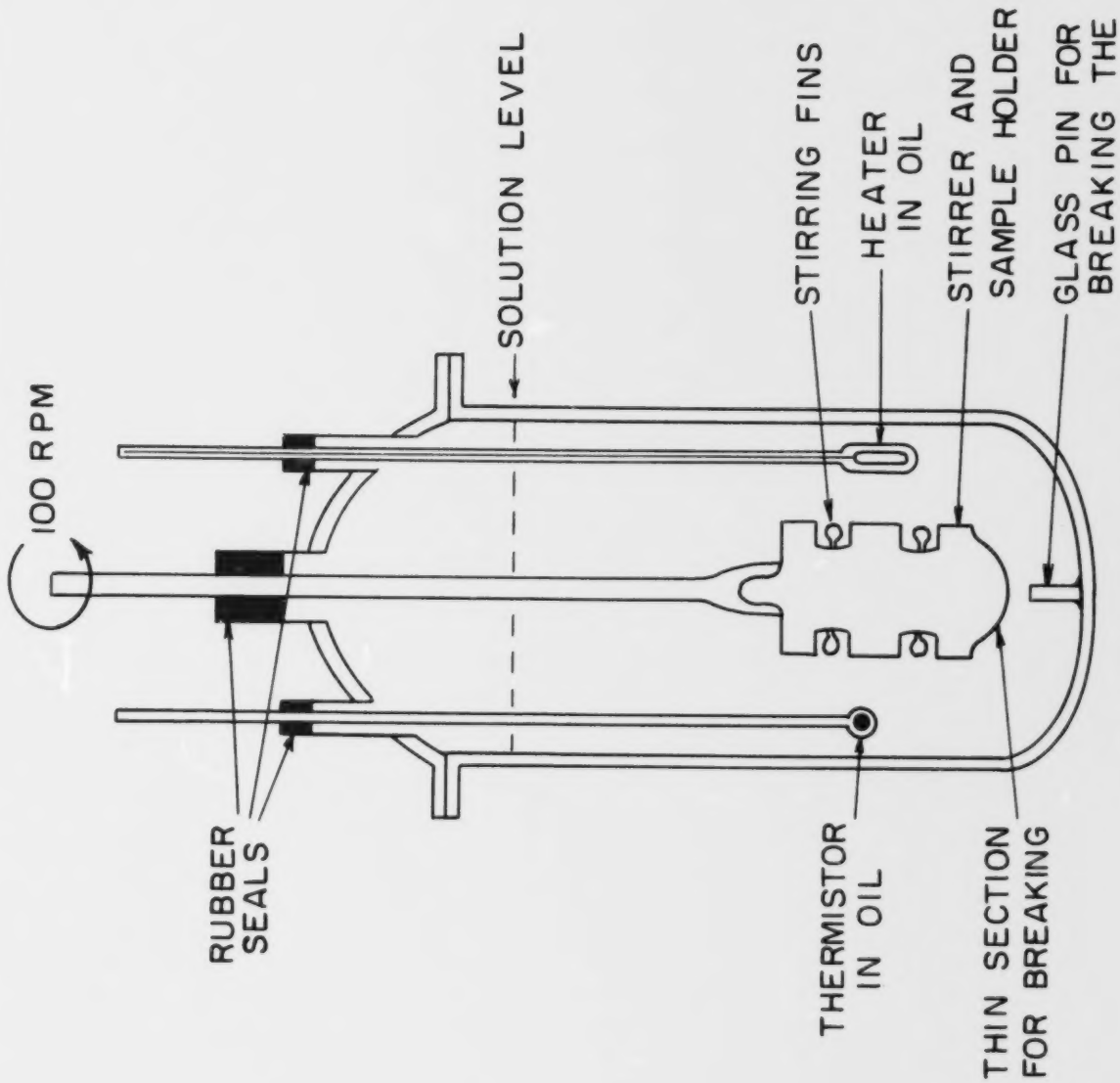

100 RPM
SOLUTION LEVEL
STIRRING FINS
HEATER IN OIL
STIRRER AND SAMPLE HOLDER
GLASS PIN FOR BREAKING THE BULB
RUBBER SEALS
THERMISTOR IN OIL
THIN SECTION FOR BREAKING

FIGURE 2

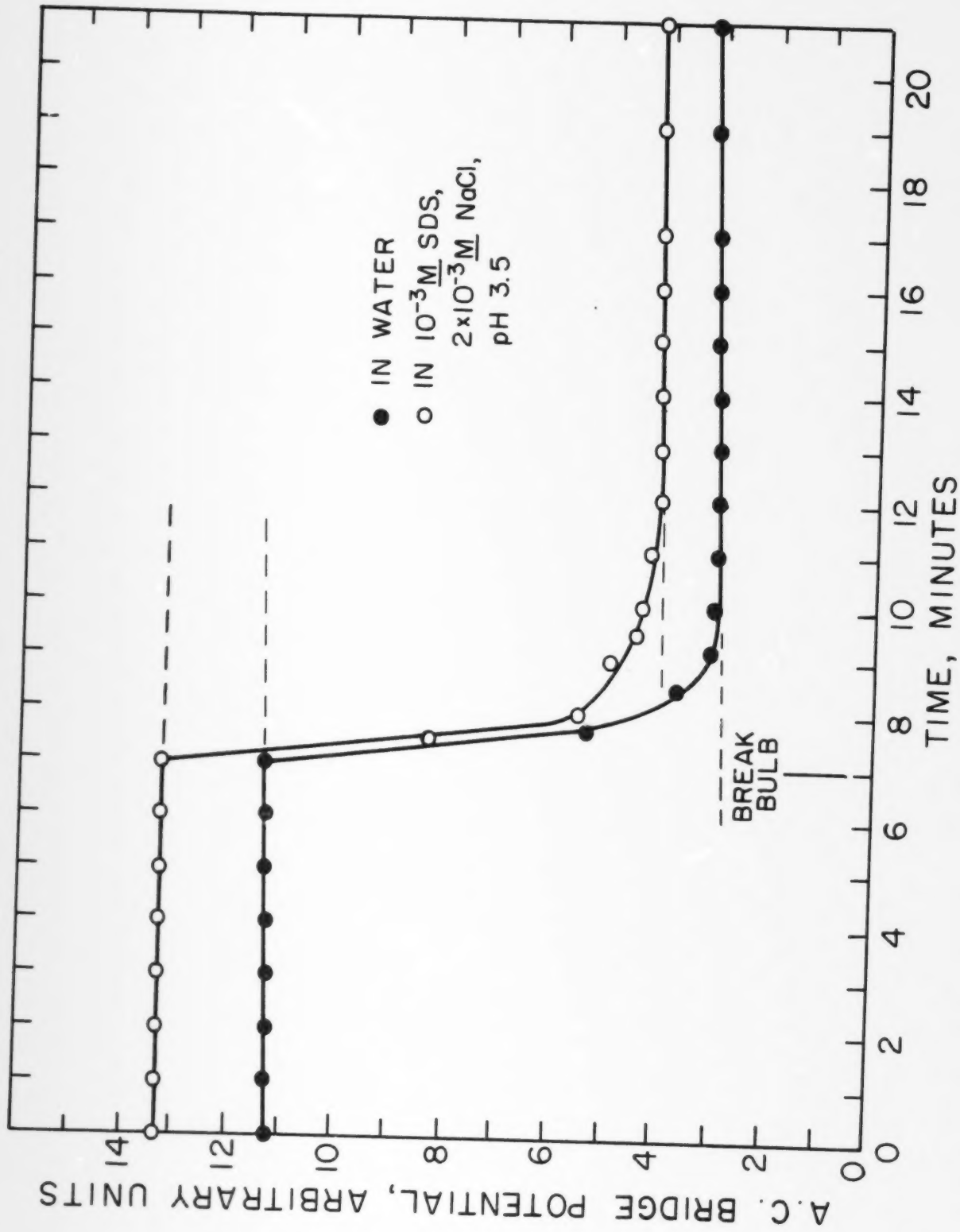

A.C. BRIDGE POTENTIAL, ARBITRARY UNITS
TIME, MINUTES
● IN WATER
○ IN 10^{-3}M SDS, 2×10^{-3}M NaCl, pH 3.5
BREAK BULB
0
2
4
6
8
10
12
14
16
18
20

FIGURE 3

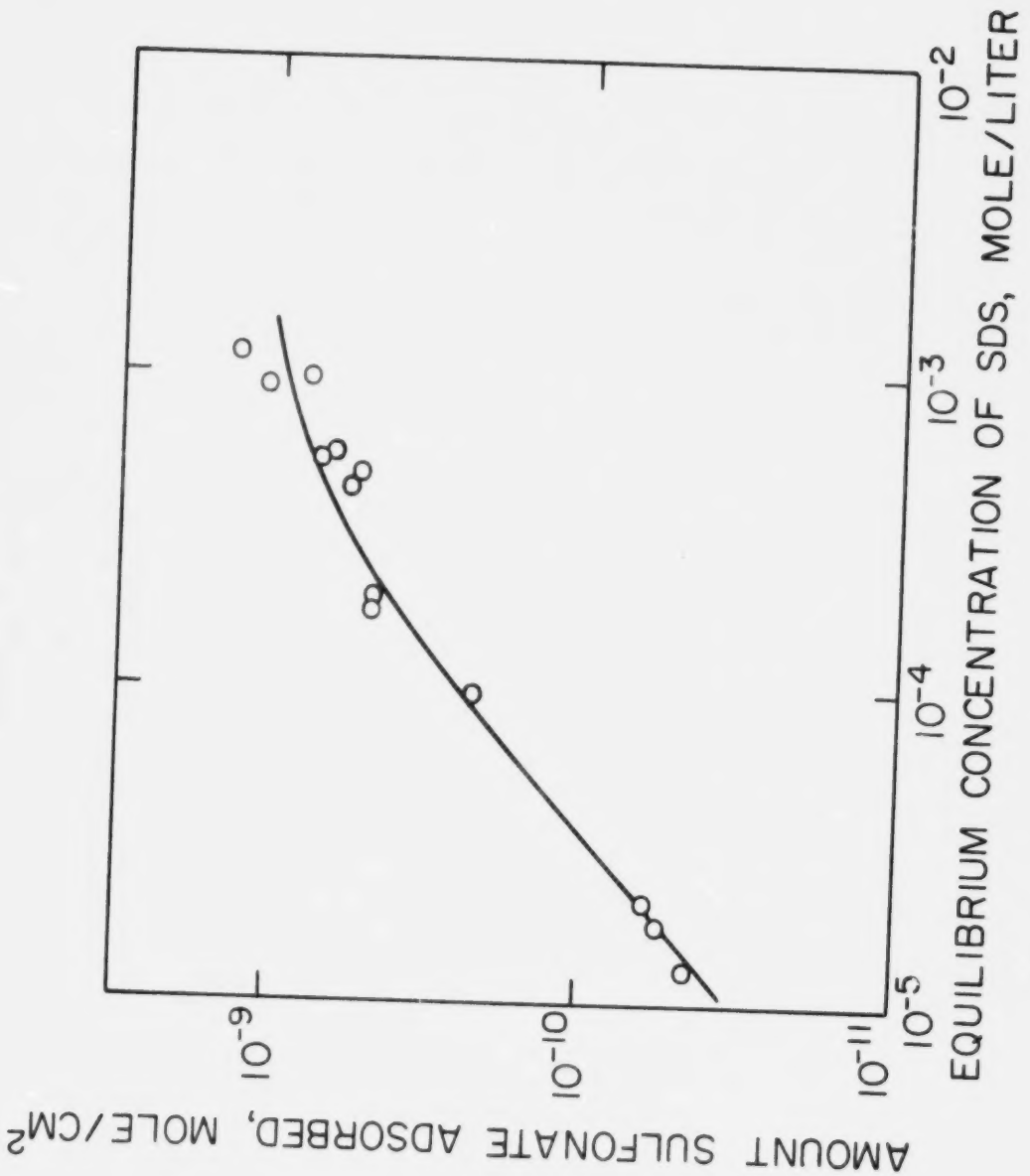

AMOUNT SULFONATE ADSORBED, MOLE/CM²
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻⁵
10⁻⁴
10⁻³
10⁻²
EQUILIBRIUM CONCENTRATION OF SDS, MOLE/LITER

FIGURE 4

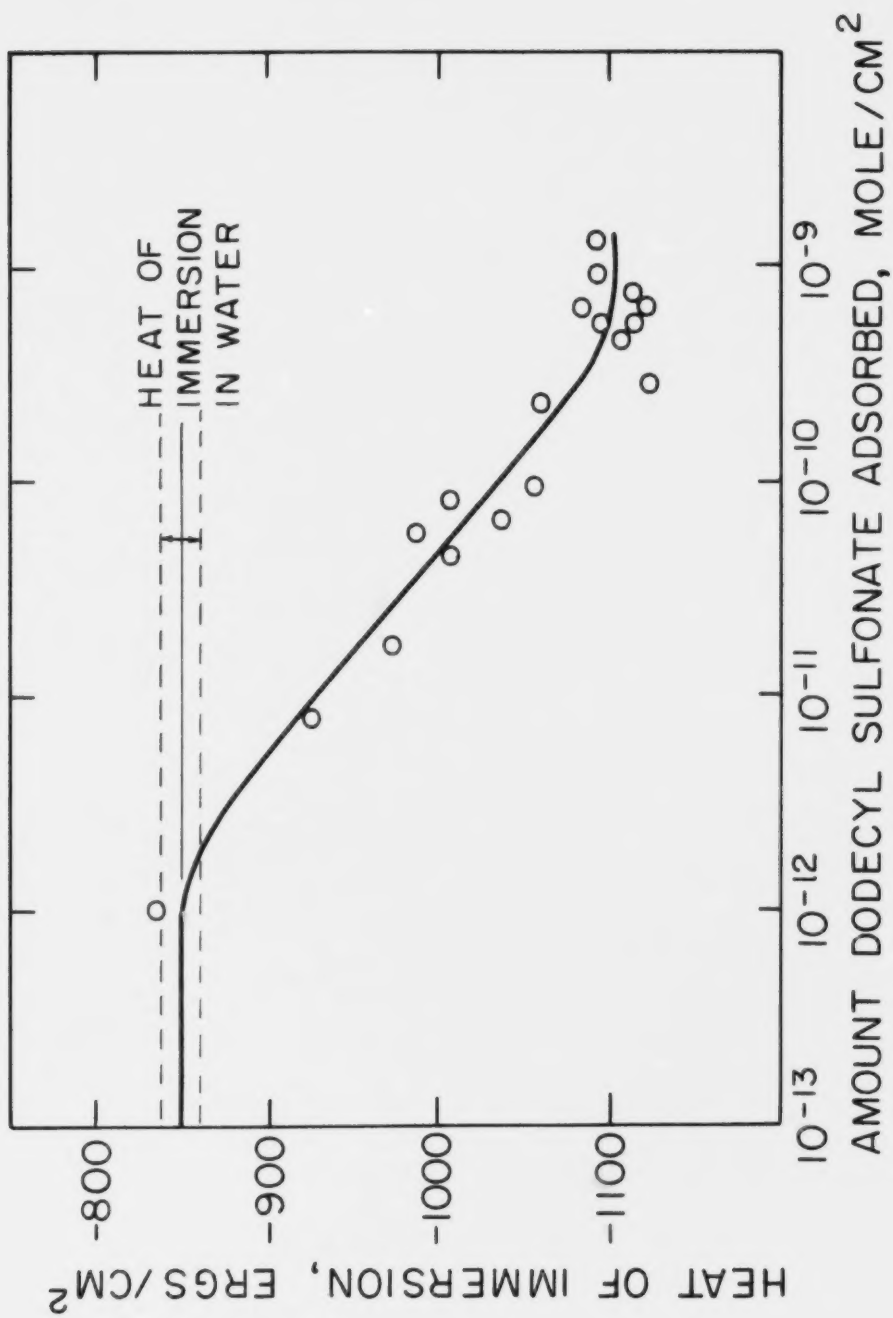

HEAT OF IMMERSION, ERGS/CM²
-800
-900
-1000
-1100
HEAT OF IMMERSION IN WATER
10⁻¹³
10⁻¹²
10⁻¹¹
10⁻¹⁰
10⁻⁹
AMOUNT DODECYL SULFONATE ADSORBED, MOLE/CM²

FIGURE 5

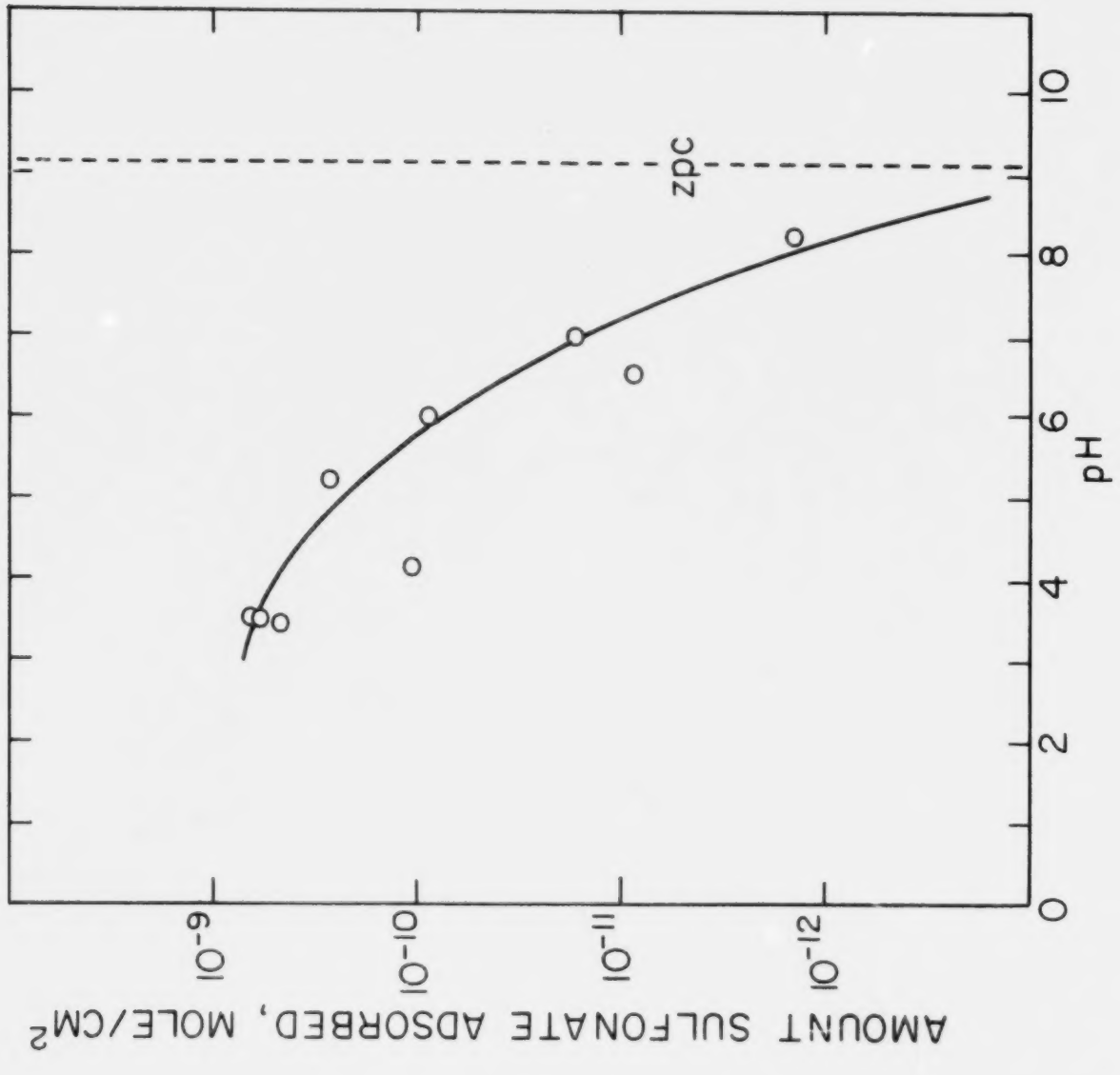
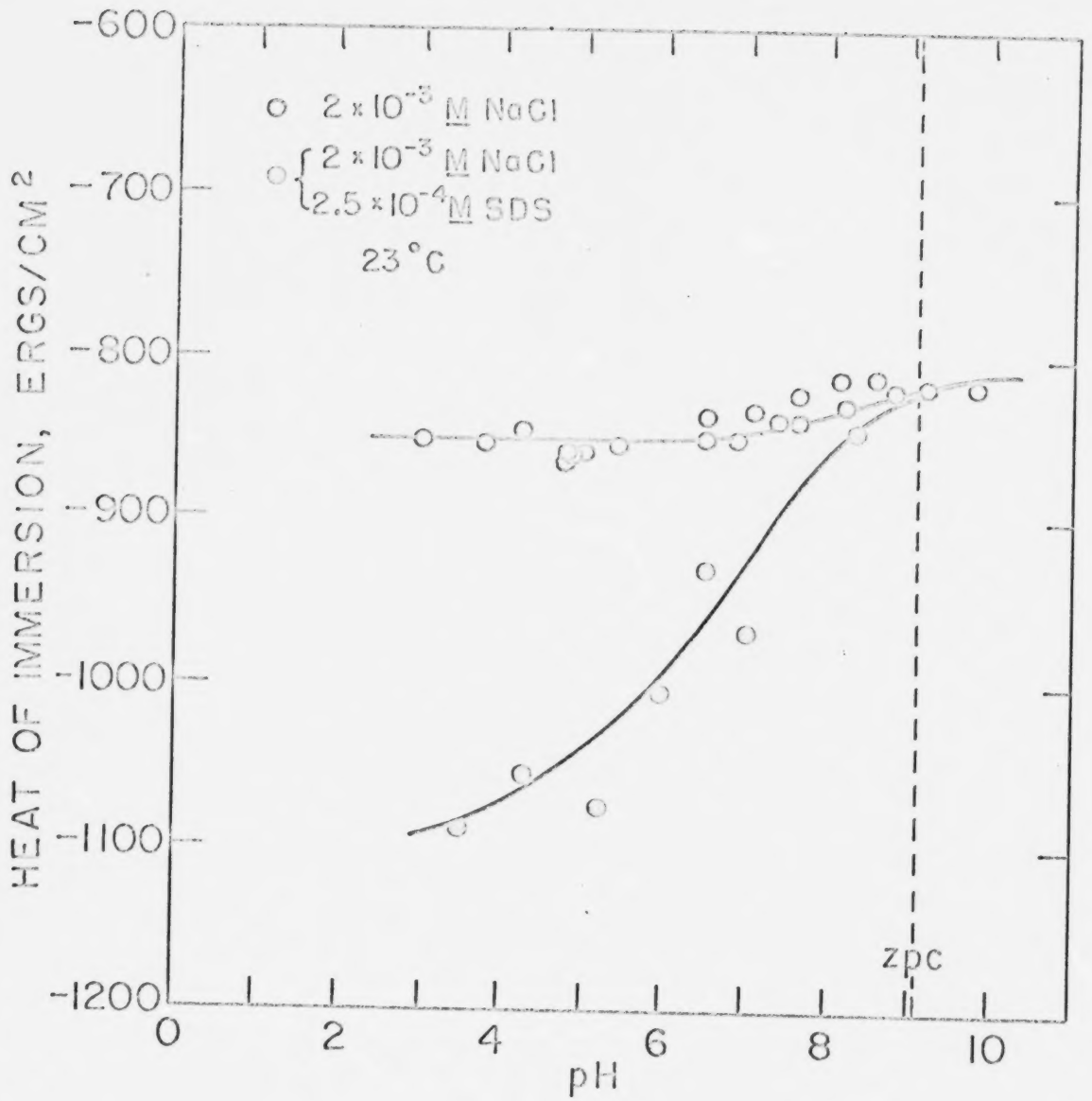

AMOUNT SULFONATE ADSORBED, MOLE/CM²
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
0
2
4
6
8
10
pH
zpc

FIGURE 6


-600
-700
-800
-900
-1000
-1100
-1200
HEAT OF IMMERSION, ERGS/CM²
o 2 x 10⁻³ M NaCl
o { 2 x 10⁻³ M NaCl
2.5 x 10⁻⁴ M SDS
23 °C
zpc
0
2
4
6
8
10
pH

SECTION 4

THE ADSORPTION OF ALKYBENZENE SULFONATES AT THE ALUMINA-WATER INTERFACE

ABSTRACT

The benzene ring in alkylaryl sulfonates is important in adsorption at solid-water interfaces in two distinct ways. It increases the adsorption potential by an amount equivalent to adding three CH_2 groups to the alkyl chain and it imparts pH insensitivity to the adsorption process. This investigation has shown that ABS-type surfactants adsorb in accord with the hemimicelle hypothesis. Data on the adsorption and coagulation behavior of commercial sodium dodecylbenzene sulfonate are also presented.

INTRODUCTION

With the increase in the use of biodegradable detergents and the subsequent lowering of the ABS level in natural waters there has been less attention focused on the interaction of ABS with colloidal solids. Nevertheless there are three general reasons for further examining the mechanism of ABS adsorption.

1. Adsorption models for ABS retention on enzyme surfaces in activated sludge and specific bacterial cultures are restricted to qualitative descriptions. No quantitative data on the adsorption step itself are available.
2. The mechanism adsorption of a variety of amphipathic (polar-nonpolar) molecules in water treatment and renovation processes is poorly understood. The precise roles played by the polar group (e.g. -OH, -COOH, $-SO_3$ Na or $-NO_2$), the aromatic center and the alkyl chain are uncertain. This applies to aromatic alcohol (e.g. phenol) abstraction and removal, ABS degradation, organic color removal and so on.
3. The removal of micro-organisms from water systems by flotation techniques is becoming increasingly important. In this process the function and eventual fate of added collector is yet to be defined carefully.

The various alkylbenzene sulfonate molecules offer a unique system for the study of the role of organics in water renovation. They are made up of an alkyl chain of variable structure, a simple aromatic center and a polar ionic head group. Our substrate, α-alumina, while of limited practical significance is however a colloidal solid of known surface properties and one that has been described quantitatively in our laboratories and elsewhere. It provides the organic molecule with a definite series of adsorption sites and is therefore an ideal model system that will be of considerable value in the interpretation of the adsorption of a wide variety of organic species on naturally occurring inorganic and organic substrates.

The present section of the report is concerned with the adsorption behavior of a variety of branched and straight chain ABS detergents at the alumina-water interface.

EXPERIMENTAL

The ABS detergents are of three varieties:

1. A set of alkylbenzene sulfonates of total chain lengths of 9, 10, and 12 carbons supplied by courtesy of Dr. R. D. Swisher of the Monsanto Chemical Company(1).
2. A set of C_{12}-benzene sulfonates in which the benzene sulfonate nucleus is located at the 2:10, 3:9, and 6:6 positions.
3. A commercial sodium dodecylbenzene sulfonate containing a mixture of isomers.

The various organic molecules were added to the alumina dispersions at appropriate concentrations, pH values, and total ionic strengths and conditioned in a thermostated vessel with provision for pH electrodes, sample removal and reagent addition inert gas inlet and thermometer.

Analysis of the residual ABS after adsorption was obtained by standard methylene blue methods* in some cases supplemented by standard ultra-violet spectrophotometric techniques. Calibration graphs enabled the amount of ABS adsorbed/g. of solid to be estimated and plotted as a function of concentration, pH, or ionic strength.

Electrophoresis determinations of the change in surface charge of the alumina with adsorbed organic ions were conducted on a Zeta Meter

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*In this regard it has been found that the instability of the methylene blue-ABS complex reported by other workers may be related to inefficient abstraction. A report on this aspect is to be prepared.

apparatus. Changes in coagulation behavior of the alumina dispersions due to changes in adsorption of the organic were followed on a recording spectrophotometer by monitoring the changes in scattered light intensity.

RESULTS AND DISCUSSION

In a series of continuing investigations in these laboratories a quantitative description of the mechanism of alkyl surfactant adsorption on various substrates has been built up[2-6]. The adsorption behavior has been interpreted in terms of the following model:

> Region 1. At low concentrations the organic surfactant ion adsorbs on isolated, probably high energy, sites at the interfaces. There is considerable rotational freedom for the surfactant molecules and negligible interaction with its neighbors.
>
> Region 2. The second region is marked by an abrupt increase in adsorption and the approach to zero electrokinetic potential. The concentration in solution (i.e. equilibrium concentration) is called the hemimicelle concentration, in that two dimensional association takes place between adsorbed surfactant ions via van der Waals interaction between the alkyl chains.
>
> Region 3. The final adsorption region involves reversal of charge of the colloidal substrate by the adsorbed organic ion and approach to monolayer and then multilayer adsorption.

The detailed nature of the adsorption of these alkyl surfactants and the corresponding surface charge and coagulation behavior are discussed in References 2 through 6. It is therefore important to compare and contrast the adsorption of ABS in terms of this detailed mechanism.

Effect of Chain Branding on the Adsorption of Sodium Dodecylbenzene Sulfonate

The adsorption isotherms (25°C) of the 2-10, 3-9, and 6-6 isomers of sodium C_{12} benzene sulfonate are shown in Figures 1, 2, and 3. The supporting electrolyte was 5×10^{-4} M KCl for all experiments and the

adsorption was followed for various constant pH conditions ranging from about pH 4 to pH 7. At the high concentration end of the isotherms of the 2-10 isomer the data points superimpose within experimental error.

The role of pH at constant added concentrations of each isomer is shown in Figure 4. While it is more strictly correct to plot these pH isotherms for constant equilibrium concentrations, for most practical purposes it is more important to represent the data as shown in Figure 4, namely, in terms of constant added ABS.

On comparison of these ABS adsorption data with that previously obtained with alkyl surfactants it can be seen that <u>again</u> there is an abrupt change in adsorption, Region 1 and Region 2, in every case. Since the pure reagents used were available in limited quantities it was not possible to proceed to concentrations beyond about 10^{-4} <u>M</u>. This is also unnecessary since organic levels in natural water systems and processes are in fact well below this upper limit of 10^{-4} <u>M</u>. The hemimicelle concentrations indicated by the abrupt breaks in the isotherms again occur at some 100 fold lower concentrations than is found for micelle formation in bulk solutions.

In contrast with the adsorption of alkyl surfactants which show dramatic pH dependence of the adsorption, the ABS adsorption is notably independent of pH over a wide range. Thus the introduction of the aromatic nucleus has added a surface charge insensitive adsorption force. Some tail-off at pH values just below the zero-point-of-charge (zpc) of this alumina (pH 8.4) is observed and further, minimum adsorption above the pH of the zpc was observed.

The displacement to lower amounts adsorbed (i.e. for fixed amounts in solution) of the 3-9 from the 2-10 and the 6-6 from the 3-9 isomers confirms that chain branching will restrict alkyl chain association in the adsorbed layer. Thus it is also apparent that while chain

branching does not markedly affect the amount adsorbed at the hemimicelle concentration it does greatly affect the hemimicelle concentration itself. For example, at pH 6.0-6.1 the hemimicelle concentration shifts from 5×10^{-6} for the 2-10 isomer to 1.5×10^{-5} for the 6-6 isomer, but the amount adsorbed is unaltered at around 1.5×10^{-7} moles/g. of alumina.

Effect of Alkyl Chain Length on ABS Adsorption

The complete adsorption isotherms for C_{12}, C_{10}, and C_9 alkylbenzene sulfonates (supplied by Swisher[1]) are shown in Figure 5. The assignments of Regions 1, 2, and 3 along each region of each isomer are based on the previous alkyl sulfonate studies[5, 6] and on the electrophoretic mobility data shown in Figure 6 for the C_{10} and C_{12} isomers.

It is especially interesting to compare the C_9 alkyl benzene sulfonate isotherm with that of the C_{12} alkyl sulfonate previously reported[5, 6]. The dotted line on Figure 5 is the adsorption isotherm of sodium dodecyl benzene sulfonate on the same alumina at the same pH and ionic strength. This general equivalence between a C_n alkylbenzene sulfonate and a $C_{(n+3)}$ alkyl sulfonate illustrated in Figure 5 for adsorption at a solid substrate-water interface is the exact parallel to that reported[7] for the critical micelle concentrations of alkylbenzene and alkyl sulfonates in bulk solution.

The closeness of this parallel must now be interpreted in terms of the pH effect on adsorption shown in Figure 4. Despite the fact that a benzene ring contributes three CH_2 groups, in effect, of adsorption potential, its role must be more complex since its presence destroys the marked pH dependence of the adsorption of normal non-aromatic surfactants. At present it is uncertain as to the detailed role played by the benzene ring. It is probable that some overlap of the π-electron system of the ring with the electronic distribution across the surface

takes place. It is also possible that π-electron overlap is occurring between adjacent benzene rings in the two-dimensional aggregate at the solid-liquid interface. The close similarities between the form of the adsorption isotherms of alkyl and alkylaryl surfactants suggests that π overlap between adjacent close-packed benzene rings is occurring and adding 1.8-2.0 kcal/mole (i.e. three CH_2 groups) to the adsorption energy.

The electrophoretic mobility data shown in Figure 6 illustrate the enhanced adsorption and therefore charge reversal that accompanies hemimicelle formation. The shape of these mobility curves is almost exactly that expected from the same curves for alkyl detergents. The dotted curve on Figure 6 is the mobility-concentration isotherm of tetradecylammonium acetate adsorbing at the SiO_2-water interface[3] being displaced by an amount approximately equivalent to one benzene ring or three methylene groups. This superimposition of a C_{n+3} cationic organic adsorbed on SiO_2, and a C_n^- benzene anionic organic adsorbed on Al_2O_3 demonstrates the general validity of treating all organic-substrate interactions in terms of the Fuerstenau, et. al. hemimicelle model.

Adsorption of Commercial Surfactants

The particular commercial surfactant studied was an inorganic salt-free, mixed isomers, sample of sodium dodecylbenzene sulfonate. The adsorption behavior of this typical organic mixture is shown in Figure 7 in which the amount adsorbed (on a linear scale) is plotted against the amount added (on a logarithmic scale) for three different constant pH conditions as shown. Also included, and shown as a dotted line, is the coagulation behavior for this same organic mixture adsorbed on alumina at pH 5.85. At just over 10^{-5} M surfactant where the abrupt increase in adsorption is indicated there is a comparable increase in coagulation of the dispersion by adsorbed surfactant.

Similar coagulation behavior has been reported for high purity alkyl sulfonates adsorbed on α-Al_2O_3 [4]. Again the close parallel between the alkyl surfactant and alkylaryl surfactant adsorption behavior is most striking but again does not depend, as can be seen from Figure 7, to any great extent on pH.

The linear-log plot of Figure 7 illustrates quite dramatically the sharpness or critical character of hemimicelle formation in these systems. It is also interesting to compare the data shown in Figures 1, 3, and 7; the mixed organic behaves more like the pure 6-6 branched chain isomer than like the 2-10 straight chain isomer. Clearly the total adsorption depends more on the length of the alkyl chain and less on the degree of branching. This effect, unexpected from consideration of the adsorption behavior of alkyl surfactants, is again thought to be related to the nature of benzene ring-benzene ring interactions.

SUMMARY

The present study has established an important duality in the adsorption of alkylaryl surfactants onto solid substrates. On the one hand the presence of a benzene ring adds the equivalent of three CH_2 groups (approximately 2 kcal/mole) to the adsorption energy. On the other hand, it imparts pH insensitivity to the adsorption so that its role must be only partly related to hydrophobic bonding.

It is probable that the electron overlap between close-packed rings is responsible for this enhanced adsorption. The hemimicelle hypothesis has been extended to ABS type adsorption and found to be equally applicable.

The study should enable better interpretation of present and future studies on the removal of organics during water treatment and the action of collectors in micro-organism flotation.

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2. D. W. Fuerstenau, J. Phys. Chem., 60, 981 (1956).

3. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, J. Phys. Chem., 68, 3562 (1964).

4. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, J. Colloid and Interface Science, 22, 599 (1966).

5. P. Somasundaran and D. W. Fuerstenau, J. Phys. Chem., 70, 90 (1966).

6. K. Shinoda, et. al., Colloidal Surfactants, Academic Press, New York, New York (1963).

LIST OF FIGURE CAPTIONS

Figure 1. Isotherms for the adsorption of sodium dodecyl-2-benzene sulfonate on alumina as a function of pH.

Figure 2. Isotherms for the adsorption of sodium dodecyl-3-benzene sulfonate on alumina as a function of pH.

Figure 3. Isotherms for the adsorption of sodium dodecyl-6-benzene sulfonate on alumina as a function of pH.

Figure 4. The effect of pH on the adsorption of various isomers of sodium dodecylbenzene sulfonate on alumina at fixed additions of surfactant.

Figure 5. The effect of the alkyl chain length on the adsorption of linear alkylbenzene sulfonates onto alumina at pH 7.2.

Figure 6. The effect of surfactants on charge reversal, as indicated by electrophoretic mobilities.

Figure 7. The adsorption and coagulation behavior of commercial sodium dodecylbenzene sulfonate on alumina in aqueous media.

FIGURE 1

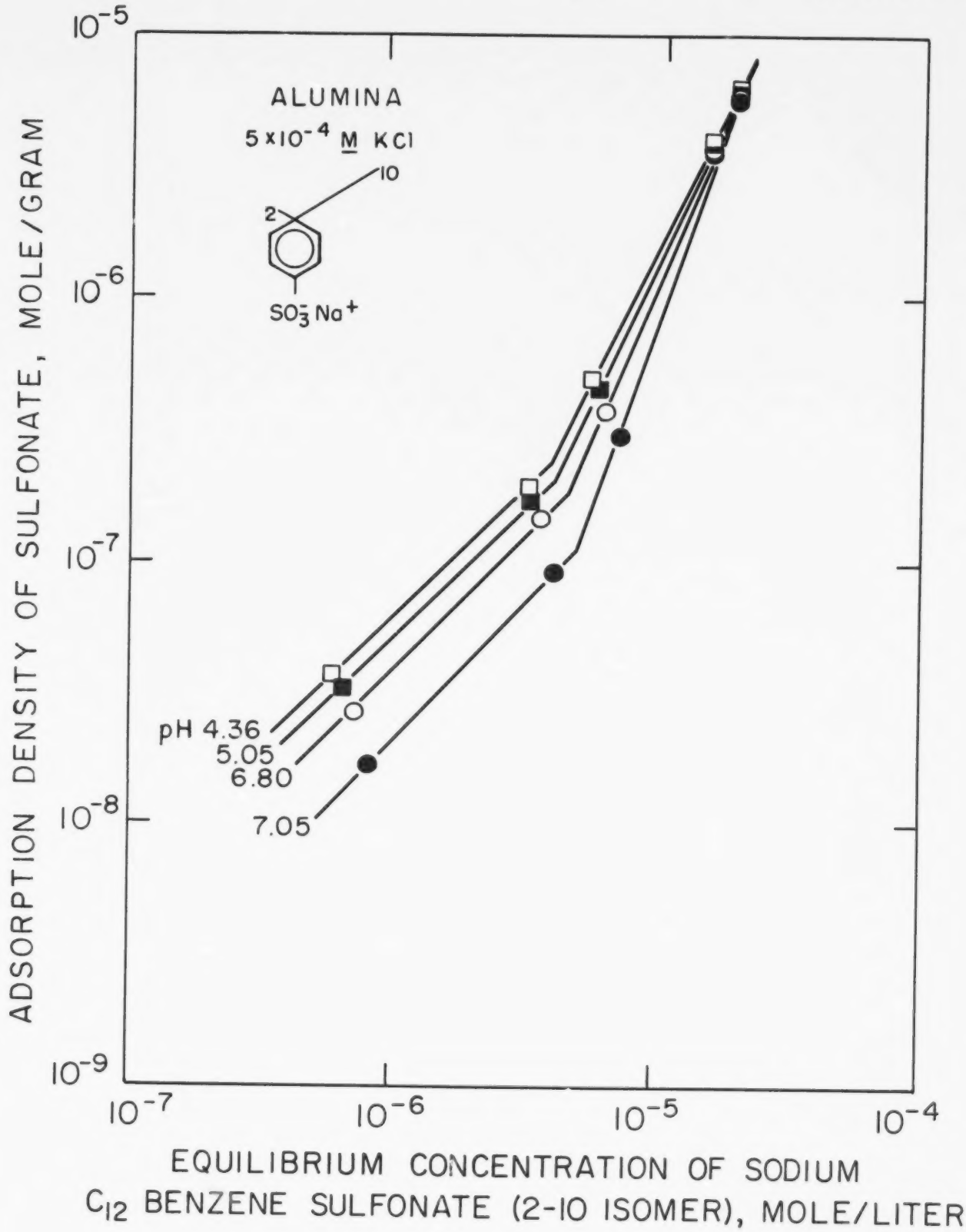

ALUMINA
5 x 10⁻⁴ M KCl
10
2
SO₃⁻ Na⁺
pH 4.36
5.05
6.80
7.05
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
10⁻⁷
10⁻⁶
10⁻⁵
10⁻⁴
ADSORPTION DENSITY OF SULFONATE, MOLE/GRAM
EQUILIBRIUM CONCENTRATION OF SODIUM
C12 BENZENE SULFONATE (2-10 ISOMER), MOLE/LITER

FIGURE 2

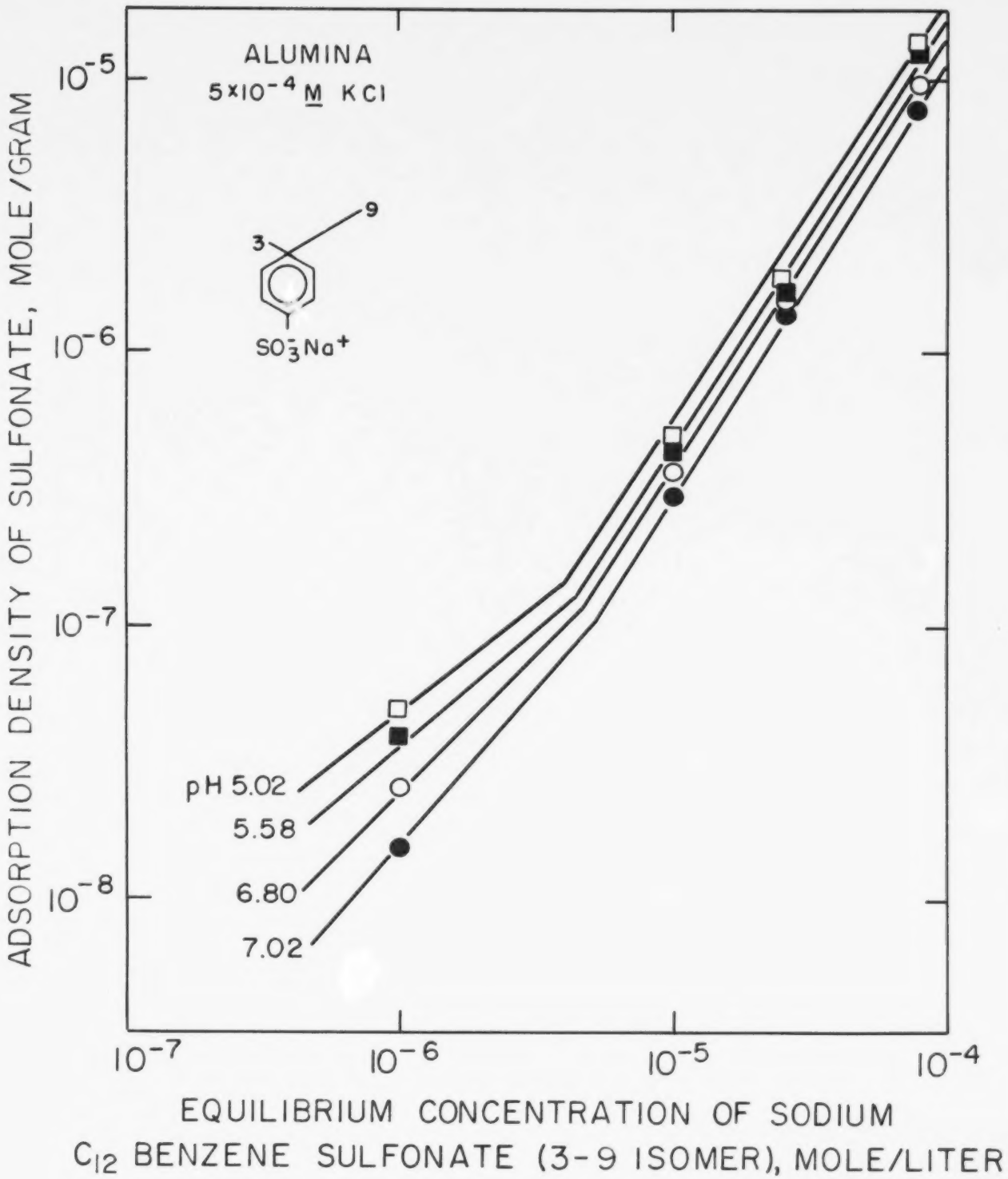

ALUMINA
5×10⁻⁴ M KCl
9
3
SO₃⁻Na⁺
pH 5.02
5.58
6.80
7.02
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
ADSORPTION DENSITY OF SULFONATE, MOLE/GRAM
10⁻⁷
10⁻⁶
10⁻⁵
10⁻⁴
EQUILIBRIUM CONCENTRATION OF SODIUM
C12 BENZENE SULFONATE (3-9 ISOMER), MOLE/LITER

FIGURE 3

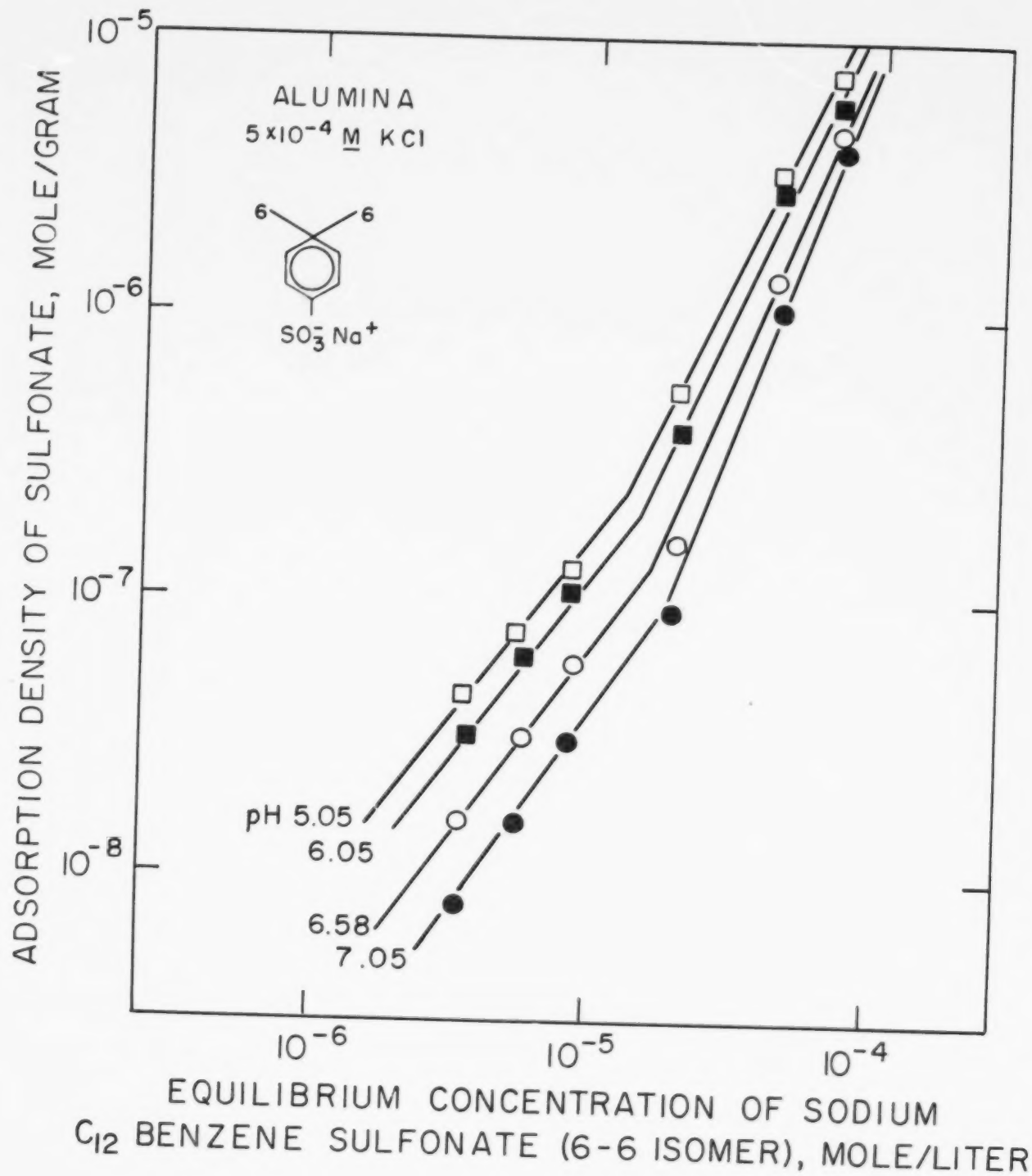

ALUMINA
5x10⁻⁴ M KCl
6
6
SO₃⁻ Na⁺
pH 5.05
6.05
6.58
7.05
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁶
10⁻⁵
10⁻⁴
ADSORPTION DENSITY OF SULFONATE, MOLE/GRAM
EQUILIBRIUM CONCENTRATION OF SODIUM
C12 BENZENE SULFONATE (6-6 ISOMER), MOLE/LITER

FIGURE 4

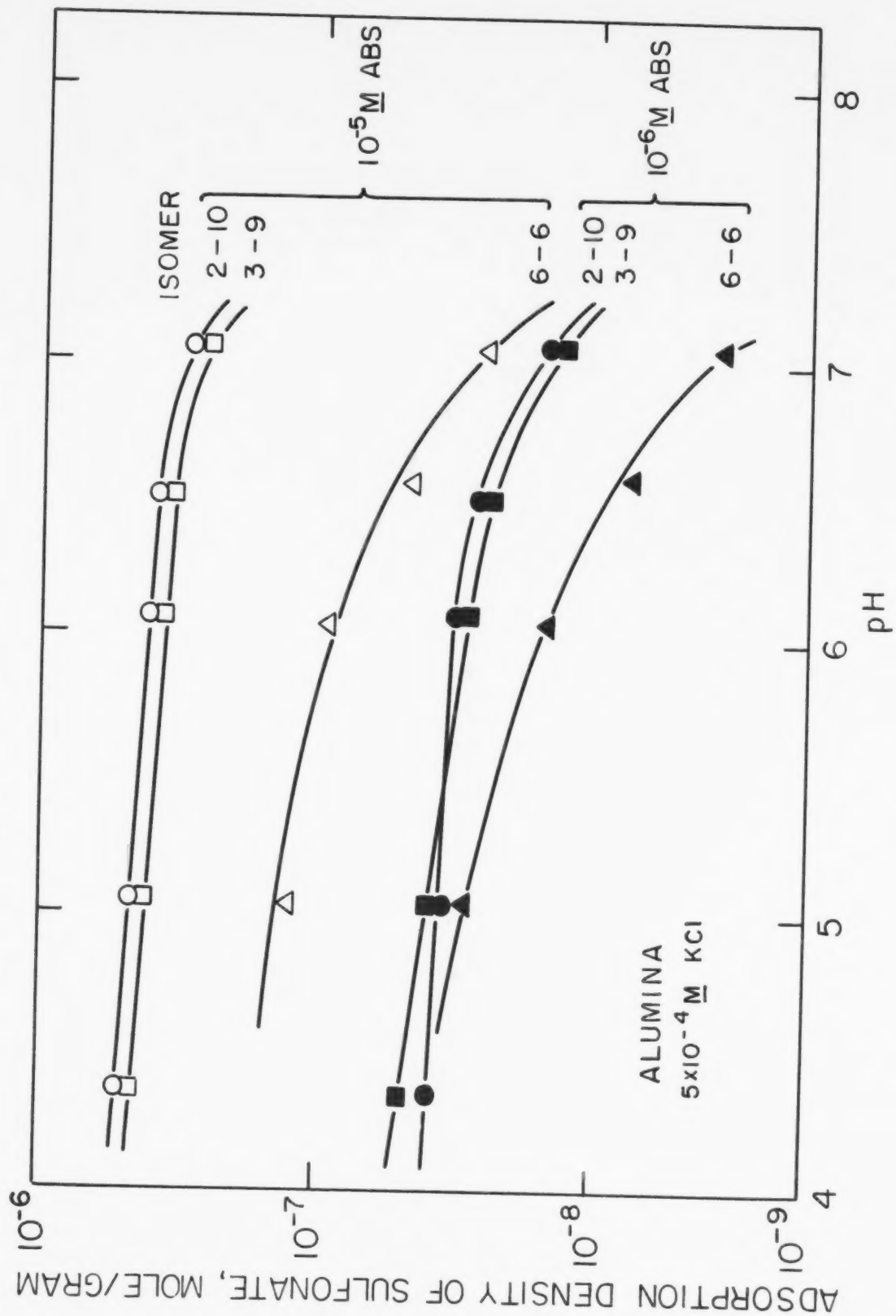

ADSORPTION DENSITY OF SULFONATE, MOLE/GRAM
10-6
10-7
10-8
10-9
4
5
6
7
8
pH
ALUMINA
5x10-4 M KCl
ISOMER
2-10
3-9
6-6
10-5 M ABS
2-10
3-9
6-6
10-6 M ABS

FIGURE 5

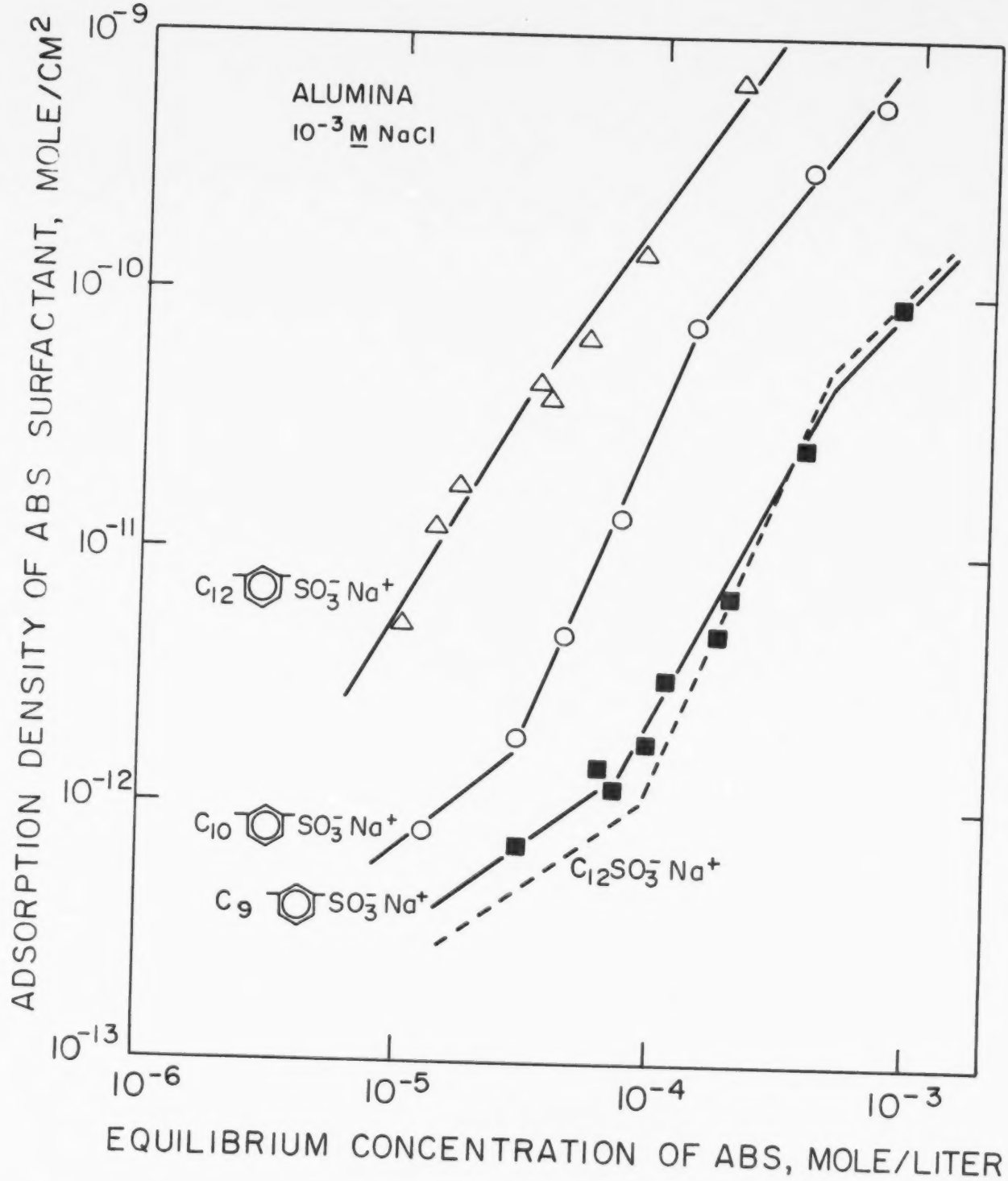

ALUMINA
10^{-3} M NaCl
C_{12} SO_3^- Na^+
C_{10} SO_3^- Na^+
C_9 SO_3^- Na^+
$C_{12}SO_3^-$ Na^+
ADSORPTION DENSITY OF ABS SURFACTANT, MOLE/CM^2
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
EQUILIBRIUM CONCENTRATION OF ABS, MOLE/LITER

FIGURE 6

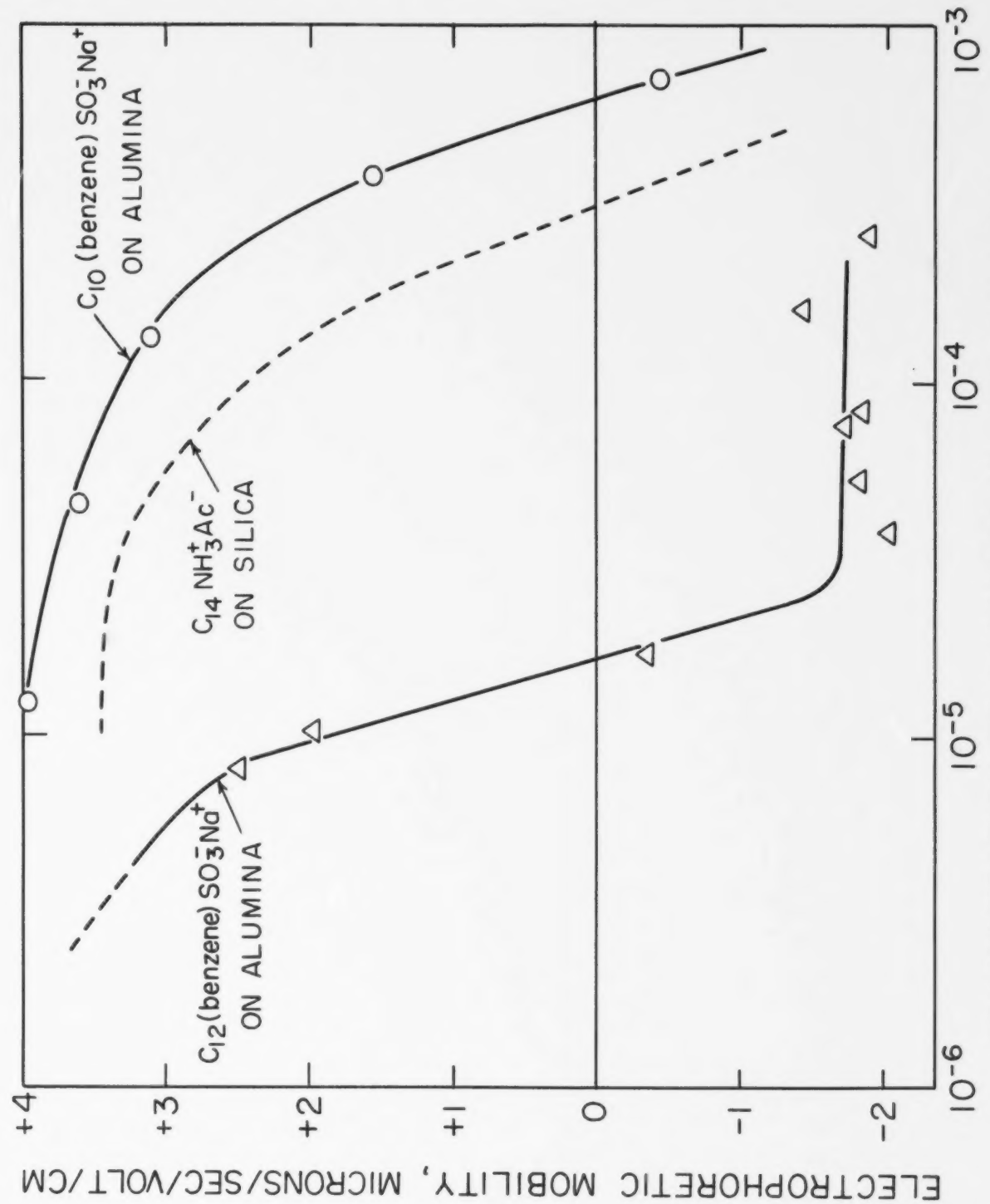
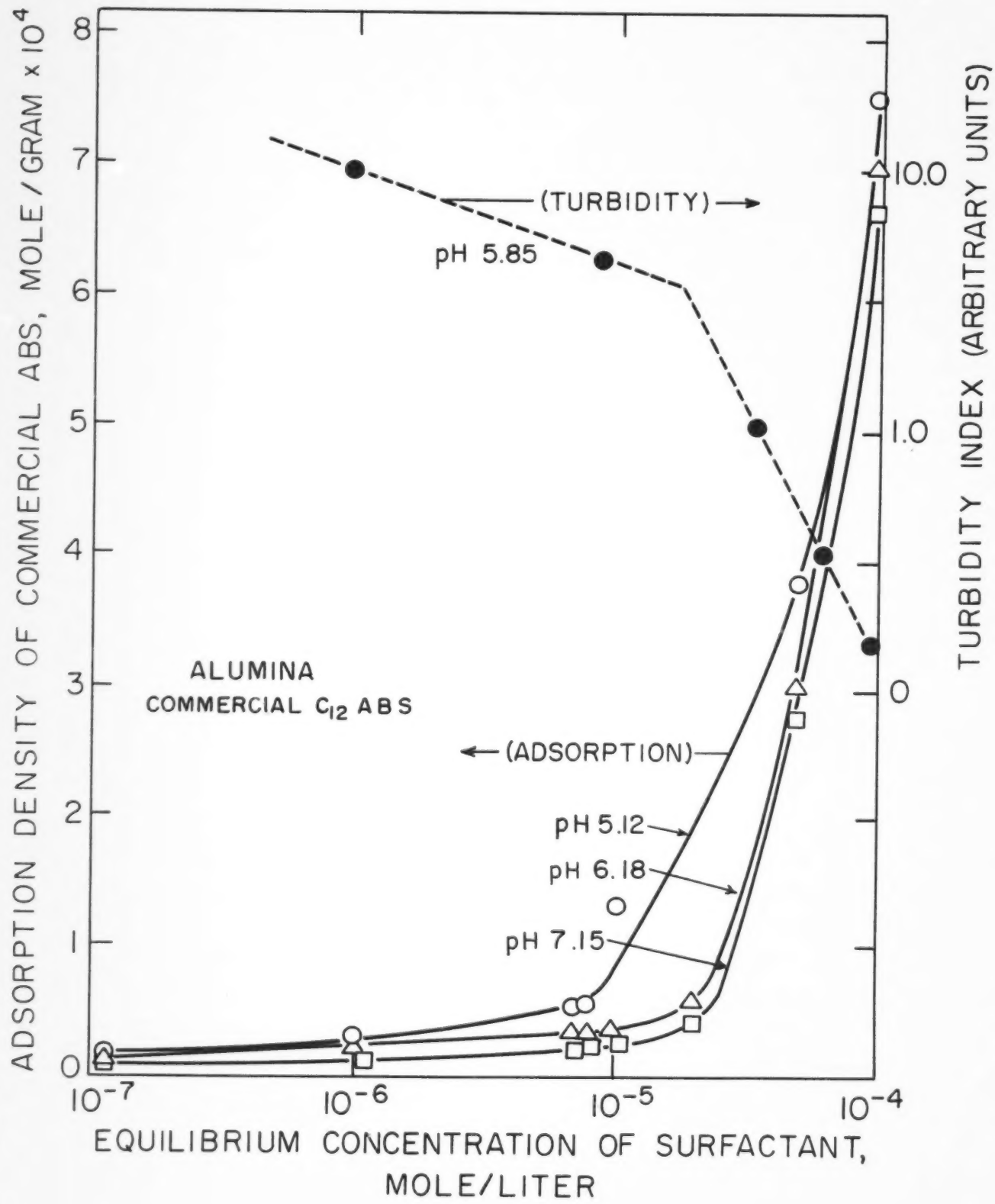

ELECTROPHORETIC MOBILITY, MICRONS/SEC/VOLT/CM
+4
+3
+2
+1
0
-1
-2
10^{-6}
10^{-5}
10^{-4}
10^{-3}
CONCENTRATION OF SURFACTANT, MOLE/LITER
C_{10} (benzene) $SO_3^-Na^+$ ON ALUMINA
C_{14} $NH_3^+Ac^-$ ON SILICA
C_{12}(benzene) $SO_3^-Na^+$ ON ALUMINA

FIGURE 7


ADSORPTION DENSITY OF COMMERCIAL ABS, MOLE / GRAM x 10^4
TURBIDITY INDEX (ARBITRARY UNITS)
(TURBIDITY) →
pH 5.85
ALUMINA
COMMERCIAL C_{12} ABS
← (ADSORPTION)
pH 5.12
pH 6.18
pH 7.15
10^{-7}
10^{-6}
10^{-5}
10^{-4}
EQUILIBRIUM CONCENTRATION OF SURFACTANT, MOLE/LITER

SECTION 5

THE EFFECT OF SURFACE CHARGE ON THE ADSORPTION OF SODIUM DODECYL SULFONATE BY AN OXIDE ADSORBENT

In systems where detergents are adsorbed as counter ions within the electrical double layer at the adsorbent-water interface, surface charge should play a vital role in determining the extent of detergent adsorption. If the adsorbent is an oxide material, then pH should be the most important variable in such adsorption systems. To study these concepts, the adsorption isotherms of sodium dodecyl sulfonate on Linde-A alumina as a model adsorbent were measured at various pH's with temperature and ionic strength being held constant. Experimental methods and materials were the same as those described in Section I.

Since the zero-point-of-charge of the alumina occurs at pH 9, adsorption of an anionic detergent can only be appreciable at pH values less than the zpc, namely pH 9. Observation of Figure 1 shows that isotherms for the adsorption of dodecyl sulfonate at pH's between 3.2 and 8.2 all have the three regions characteristic of detergent adsorption, namely: Region 1 in which the detergent adsorbs as individual counter ions in the double layer, Region 2 in which increased adsorption occurs because of hemimicelle formation, and Region 3 where charge reversal has occurred. As the pH is lowered, that is under conditions where the surface is more positively charged, the isotherms are systematically shifted to more dilute bulk solution concentrations. By pH 8.6, near the zpc, the adsorption has decreased markedly and the isotherm no longer has the characteristic shape discussed above.

The electrophoretic behavior of alumina for these conditions was determined and the results are presented in Figure 2. In general, these curves possess a similar shape. The first break in the mobility curve corresponds with hemimicelle formation, that is with the onset of Region 2

of the isotherms and the reversal of the sign of the mobility corresponds with the onset of Region 3 of the isotherms. The change in slope of the mobility curves at still higher concentrations results from double layer compression. Note the complete difference in the mobility curve at pH 9.5 as compared with the other curves. At this pH the surface charge is negative instead of positive because the pH of the bulk solution is above the zpc.

Figure 1 shows that the first break in the adsorption isotherms occurs at about the same surface concentration. This means that increasing the surface charge by lowering the pH has limited effect on how close together the adsorbed detergent ions must be before they begin to associate into hemimicelles. Of course, to achieve this desired surface concentration, the bulk concentration of detergent must be increased as the pH is increased.

Figure 1 also shows that the amount of adsorbed sulfonate ions required to bring about reversal of the electrophoretic mobility (the so-called charge reversal) decreases with increasing pH. At this condition, that is the transition from Region 2 to Region 3 in the isotherm, the surface charge resulting from the adsorption of H^+ is exactly counterbalanced by adsorbed sulfonate ions. Thus, one has a measure of the surface charge at this condition as a function of pH.

Complete analysis of these data will have to be carried out before the full significance of these interesting findings can be put into a form suitable for publication. The results do show that an inorganic adsorbent for detergent materials should be one that carries a high positive surface charge, particularly one with a zpc considerably above that of the detergent-containing water. Thus, from a technological viewpoint, it can readily be seen that surface properties of inorganic adsorbents must be quite well understood before they should be considered for removal of detergent-like substances from aqueous solution. Specifically, if the detergent

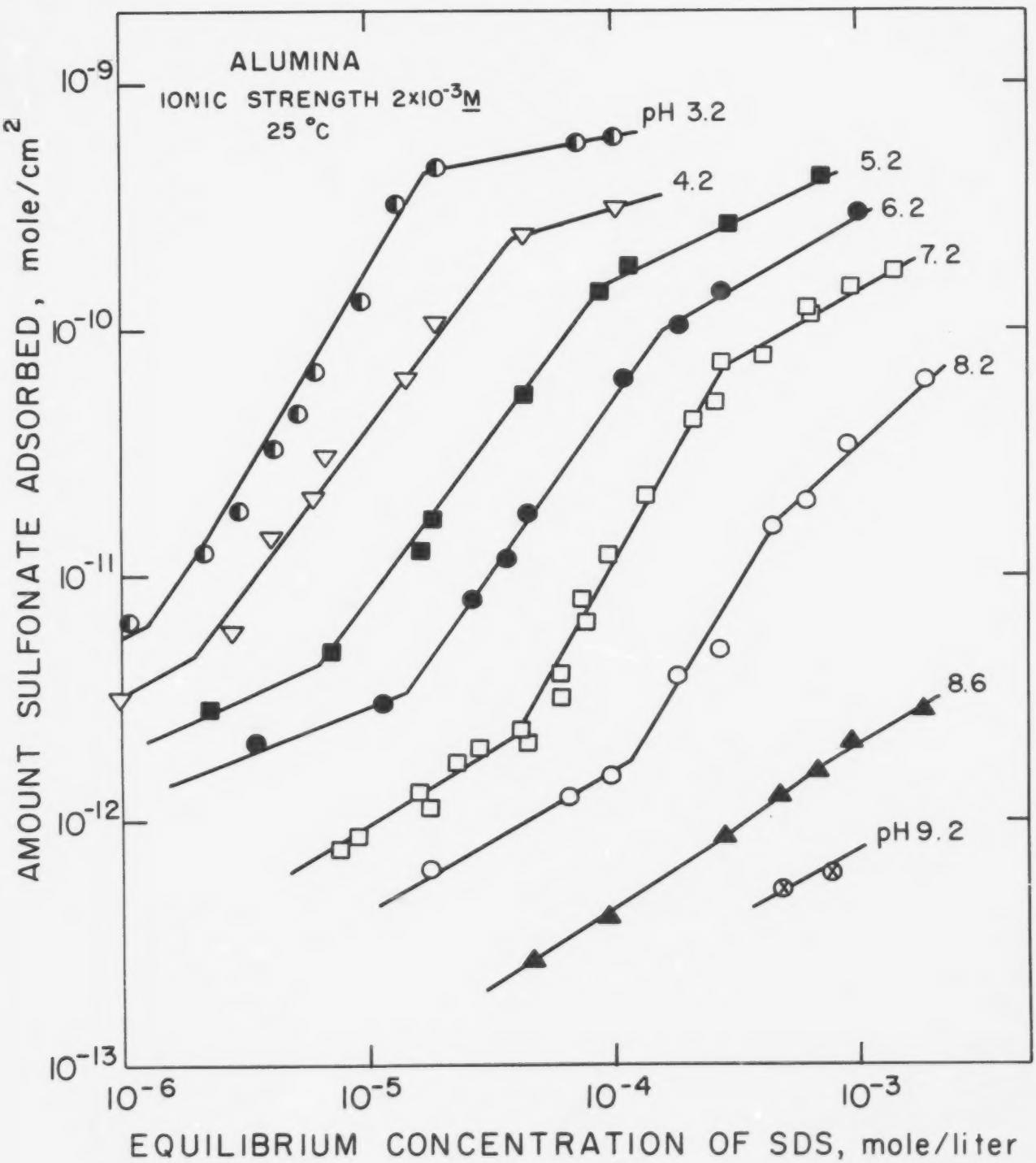
chemisorbs onto the solid surface, the sign of the surface charge is of lesser importance. But if the adsorbent is an aluminosilicate such as kaolin or other clay-like material onto which the detergent only adsorbs through physical forces, then adsorption only can be appreciable when the surface is positively charged. Unfortunately, this often is not recognized.

LIST OF FIGURE CAPTIONS

Figure 1. Isotherms for the adsorption of sodium dodecyl sulfonate on alumina at various pH's.

Figure 2. The electrophoretic mobility of alumina as a function of the concentration of sodium dodecyl sulfonate at various pH's.

FIGURE 1


ALUMINA
IONIC STRENGTH 2×10⁻³M
25 °C
pH 3.2
4.2
5.2
6.2
7.2
8.2
8.6
pH 9.2
AMOUNT SULFONATE ADSORBED, mole/cm²
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
EQUILIBRIUM CONCENTRATION OF SDS, mole/liter

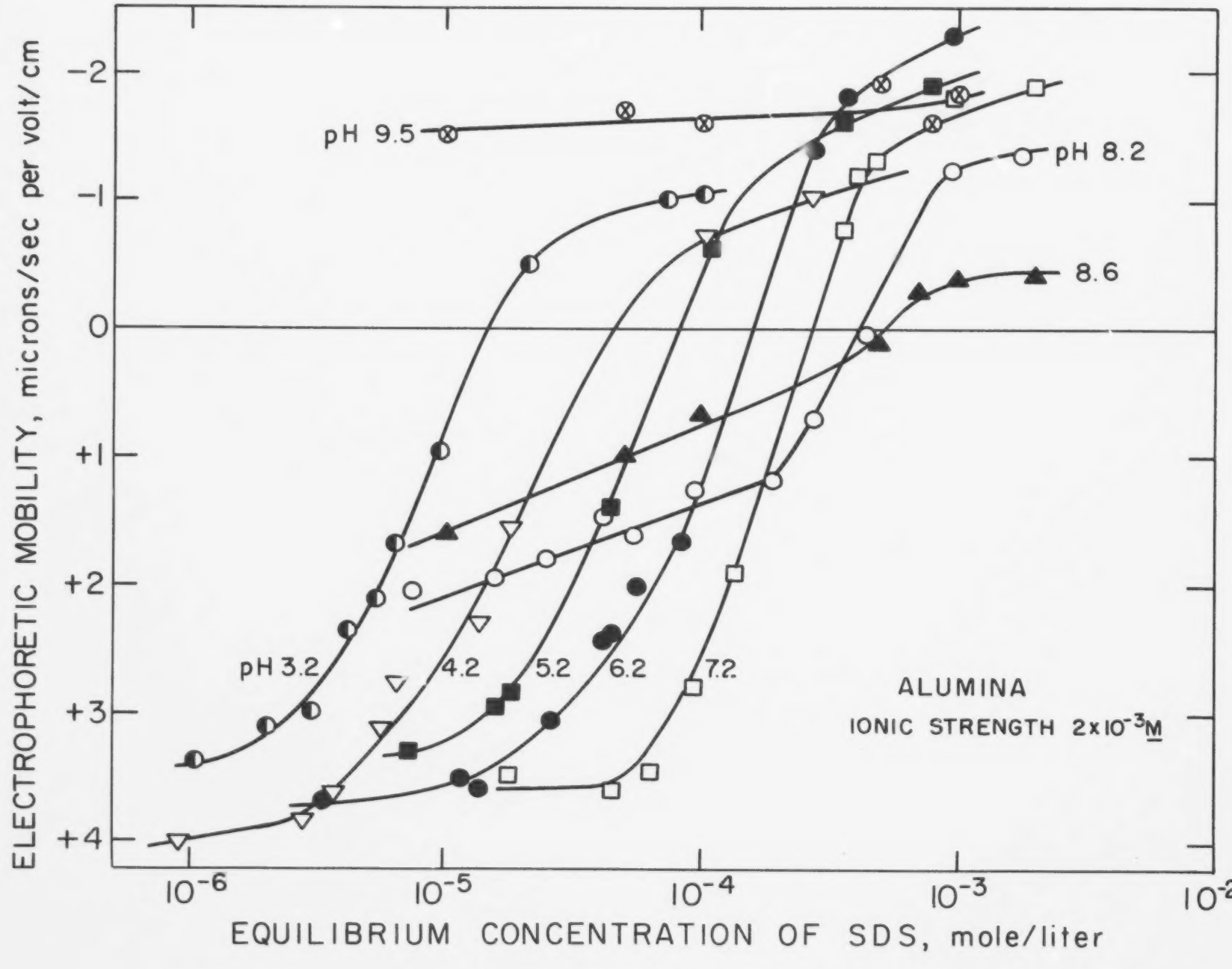

ELECTROPHORETIC MOBILITY, microns/sec per volt/cm
−2
−1
0
+1
+2
+3
+4
pH 9.5
pH 8.2
8.6
pH 3.2
4.2
5.2
6.2
7.2
ALUMINA
IONIC STRENGTH 2x10⁻³M
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
10⁻²
EQUILIBRIUM CONCENTRATION OF SDS, mole/liter

FIGURE 2

SECTION 6

THE EFFECT OF INORGANIC ELECTROLYTES ON DETERGENT ADSORPTION AT WATER-SOLID INTERFACES

Since sulfonate ions adsorb as counter ions in the electrical double layer at the interface between polar solids and aqueous solutions, inorganic electrolytes may inhibit the adsorption of detergent by competition for sites in the double layer. To study this phenomenon, the adsorption of sodium dodecyl sulfonate on alumina (Linde-A) was measured for solutions at ionic strengths of 2×10^{-4} M, 2×10^{-3} M, and 2×10^{-2} M, using sodium chloride to control the ionic strength at constant temperature and pH. The experiments were carried out utilizing methods outlined in Section 1.

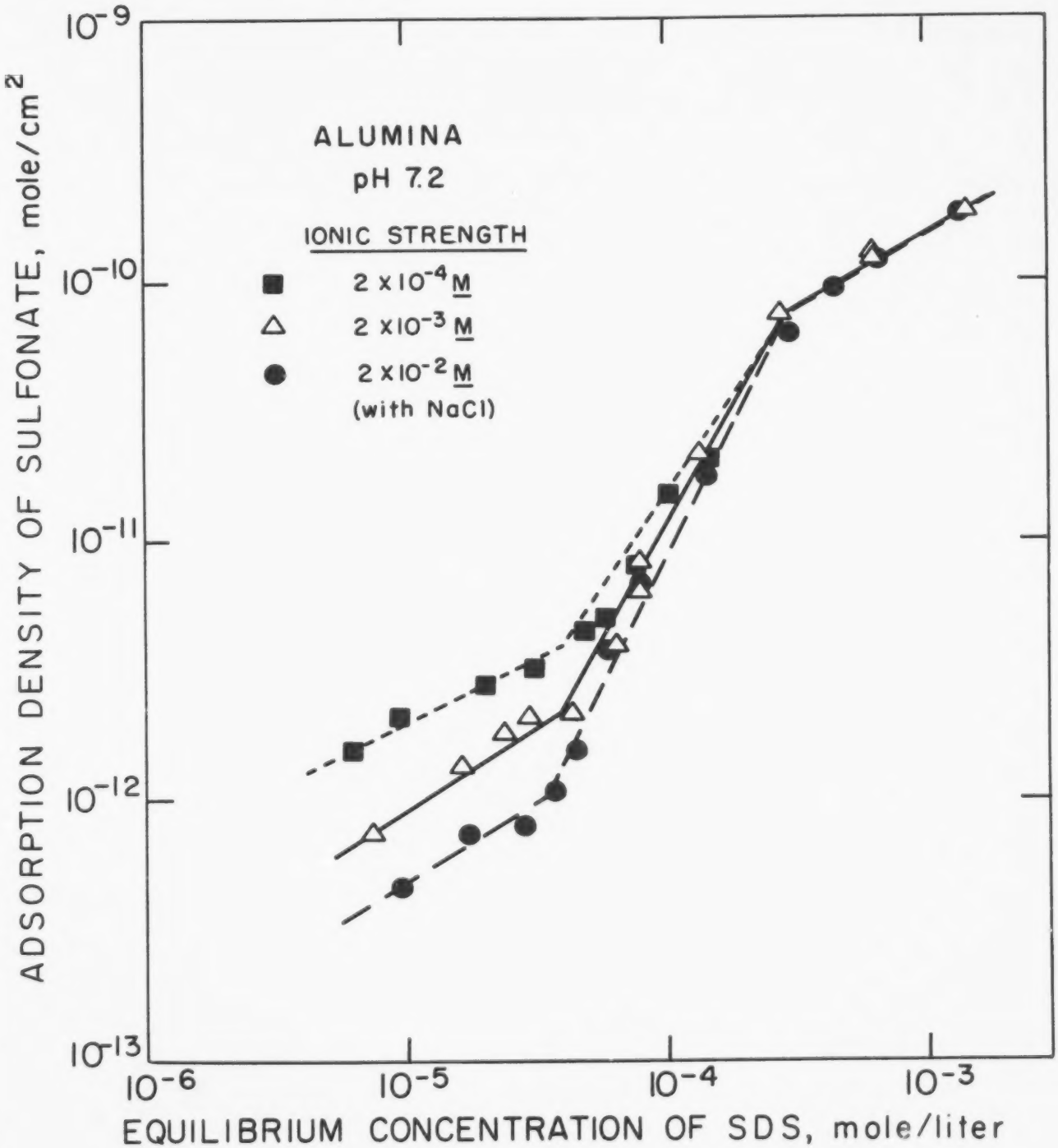
Figure 1 presents the amount of sulfonate adsorbed from solutions at these three different ionic strengths at pH 7.2 and 25°C. The results show that only in Region 1, that is where the detergent ions adsorb individually, do chloride ions compete extensively with the sulfonate ions for sites in the double layer. We had anticipated that the competition between chloride ions and sulfonate ions for the positively charged alumina surface would have been greater than that exhibited in Figure 1. Specifically, these experiments show that in Region 1 a ten-fold increase in the chloride ion concentration only decreases the sulfonate adsorption by a factor of two or so, and not by a factor of ten. In Region 2, where the specific adsorption potential due to van der Waals interaction of the hydrocarbon chains is acting, competition for surface sites strongly favors the detergent. At high sulfonate concentrations, that is in Region 3, detergent adsorption is completely independent of sodium chloride in the aqueous solution. This results because the adsorption process is controlled almost totally in this region by the van der Waals interaction of the hydrocarbon chains of the adsorbed detergent ions.

Before the role of inorganic ion competition with detergents for sites at surface can be fully understood, considerably more research will be required. For example, multivalent and hydrolyzing species undoubtedly will have much more marked competitive effects than sodium chloride, but it was not possible to extend the present investigation into this interesting area. Finally, the adsorption of all ions in the system must be determined to analyze the role of ionic strength in the adsorption process quantitatively; because of the limitations of the present work only the adsorption of the detergent itself was measured.

FIGURE CAPTION

Figure 1. Adsorption isotherms of sodium dodecyl sulfonate on alumina at ionic strengths of 2×10^{-4} M, 2×10^{-3} M, and 2×10^{-2} M.

FIGURE 1


ALUMINA
pH 7.2
IONIC STRENGTH
2 x10⁻⁴ M
2 x10⁻³ M
2 x10⁻² M
(with NaCl)
ADSORPTION DENSITY OF SULFONATE, mole/cm²
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
EQUILIBRIUM CONCENTRATION OF SDS, mole/liter

SECTION 7

GENERAL SUMMARY

In the foregoing sections of the report, the results of research into several fundamental aspects of the adsorption of detergents onto polar solids have been described in specific detail. As stated previously, the aims of this work were to investigate the nature of the adsorbate-adsorbent bond, the configuration of the adsorbed molecule, the thermodynamics of the process, and the effects of changes in the adsorbate, the adsorbent and the solution medium on the adsorption phenomena.

It has been shown that anionic detergents adsorb on polar solids such as alumina through mechanisms which are completely analogous to those responsible for the adsorption of cationic surfactants, such as amine salts, onto quartz. Thus, in general the detergents are physically adsorbed as counter ions in the electrical double layer at the surface of positively charged solid particles. At higher detergent concentrations, the simple electrostatic forces are supplemented by interactions of the van der Waals-London type between the hydrocarbon chains of the adsorbed species. Studies of the thermodynamics of detergent adsorption using measurements of the heat of immersion into detergent solutions seem to indicate that a layer of water molecules remain between the solid surface and the adsorbed sulfonate ions. Investigations of the aggregation of suspended alumina particles have shown that the effects of surfactant adsorption can be described in terms of double layer compression and reduction of the electrokinetic (zeta) potential. The role of pH in controlling the surface properties of the adsorbent and thereby the adsorption of detergents was studied, and large effects observed. Clearly, a major requirement of a material which is to be used as an adsorbent for anionic surfactants is that it have a highly positive surface potential under the given solution con-

ditions. This requirement, while seemingly obvious,is very frequently overlooked in practice. Experiments on competition between detergents and inorganic electrolytes for adsorption sites at the interface indicate quite large effects at low detergent concentrations but very little effect at the higher concentrations where hydrocarbon chain interactions become important and dominate the process.

The results of these investigations should be of considerable value to technologists faced with the many diverse problems of water pollution control. While the conditions existing in the particular model system chosen for this research may not, in general, be directly applicable to real systems, it is felt that the knowledge which has been acquired regarding the interaction between amphipathic molecules in solution and polar solid surfaces is highly relevant to many of the extremely complex problems which do exist in water-rennovation practice.